













# SMITHSONIAN

## MISCELLANEOUS COLLECTIONS.

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"EVERY MAN IS A VALUABLE MEMBER OF SOCIETY WHO BY HIS OBSERVATIONS, RESEARCHES  
AND EXPERIMENTS PROCURES KNOWLEDGE FOR MEN."—SMITHSON.

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S. P. LANGLEY,

*Secretary S. I.*





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SMITHSONIAN MISCELLANEOUS COLLECTIONS

— 969 —

THE VARIETIES  
OF THE  
HUMAN SPECIES

PRINCIPLES AND METHOD  
OF  
CLASSIFICATION

BY  
GIUSEPPE SERGI

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COMPOSED ON THE LINOTYPE.

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## A PREFATORY NOTE.

Doctor Giuseppe Sergi, professor of Anthropology in the Royal University of Rome, Italy, has made for himself a distinguished position by the ardor with which he has pursued the branch of science which he represents and the numerous valuable contributions he has made to its literature. A brief sketch of his career will form an appropriate introduction to the summary of his doctrines of craniology which is here translated.<sup>1</sup>

Dr. Sergi was born in Messina, Sicily, in 1841. His academic education was received in the Universities of Messina and Bologna, where he devoted himself especially to the departments of comparative anatomy and the philology of the Indo-European languages. In 1880 he was appointed to the chair of Anthropology in the University of Bologna, and four years later to the same position in the Faculty of Sciences of the University of Rome. In this field he has shown much energy, having by his personal exertions founded there the Museum of Anthropology and the Laboratory for Experimental Psychology. His lectures are attended by a constantly increasing class, and on the organization of the Society of Anthropology of Rome he was chosen as its first president, which position he still holds. He is also a regular, corresponding or honorary member of many learned societies in his own and other countries, among which may be mentioned in the United States the Anthropological Society of Washington, the American Philosophical Society, and the Numismatic and Antiquarian Society of Philadelphia.

His published works have been very numerous, beginning with "Principles of Psychology," in two volumes, issued at Messina in 1874, and of which a new edition is announced for this year (1894). These writings include a wide variety of subjects in physical and psychical anthropology and in education. Some are of a popular character, but the majority are strictly scientific and have been

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<sup>1</sup> *Le Varietà Umane. Principi e methodo di classificazione.* Di Giuseppe Sergi. Torino, 1893. 8vo, pp. 60.

issued by learned societies and journals. Of especial note have been his studies on the prehistoric peoples of the coasts of the Mediterranean; on the native tribes of Melanesia; on human degeneration and criminal anthropology; on the characteristics of the female sex; and, in American subjects, on the physical anthropology of the Fuegians, on skulls of the Omaguas, on ancient Peruvian skulls, and general considerations on American skulls. His attention has been fruitfully attracted to the pigmy races of Europe and to the varieties of the human species found in modern and ancient Russia, especially to the remains exhumed from the "kourgans," or ancient sepulchral tumuli, which exist in various districts of that state.

D. G. BRINTON.

# THE VARIETIES OF THE HUMAN SPECIES.

## PRINCIPLES AND METHOD OF CLASSIFICATION.

BY GIUSEPPE SERGI.

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### PART FIRST.—BASIS OF HUMAN CLASSIFICATION.

#### I.

In man, as in other animals, we find physical characteristics of two kinds, external and internal. The first are principally those pertaining to the cutis and certain cutaneous appendages, and include the coloring of the skin and hair, the structure and form of the hair, and also the coloring of the eyes. The chief internal characteristics are the bones from which the form and figure of all the members are taken, as well as those of the separate parts of the body clothed with soft tissues, such as muscles and fat. The cranium is the most important and most characteristic part of the entire human skeleton.

The cranium is a bony case which encloses a viscus of the first order, the brain, which in man is, in relation to the animal series, better developed, both in its forms and functions. It is known that the brain and cranium, from the embryological to the adult state, are in a parallel manner and gradually connected in evolution, and the external form of the one corresponds to that of the other. Most certainly it is not the cranium which gives form to the brain of man; it is more probable that it is the brain which moulds its organ of protection. Given hereditary conditions, we may affirm that the form of the cranium is correlative to that of the brain. If we could discover why the brain takes or has taken different forms we would possibly understand better its correspondence with the exterior structure of the cranium by which it is surrounded, though absolutely ignorant now. We might be

able to learn also what functional and especially what psychological characteristics are united to the cerebral forms which are revealed by cranial forms. All that is obscure for us, and also unexplored, because unsuspected; for in place of that, and in an inexact manner, the volume has been taken into account and therefore the weight of the brain, as being the only means of making an anthropological diagnosis of its functional value, the volume and weight corresponding to the capacity of the cranium.

But besides the cranium commonly called cerebral, there is the face, which, from the morphologic point of view, is not less important. The face has generally given more positive means for distinguishing human groups, not only on account of the coloring of the skin, but on account of the form and disposition of its parts, of the nose, of the cheeks, of the molar teeth, and on account of other characteristics which, when considered together, disclose differences not immediately revealed by the cerebral cranium.

The other parts of the skeleton also have differences more or less profound in the different ethnic groups, the stature, the length of the extremities, both absolutely and relatively to the stature and to the trunk; the thoracic form; and so on. But such differences seem little characteristic compared to those presented by the cranium and the face; until now, moreover, they have had but slight value, as should have those characteristics of classification which are merely secondary.

We are ignorant what may have been the primitive type or the primitive human types, considered in all their internal and external characteristics; that is, what skeletal forms certain ethnic groups of differently colored skin possessed; or, on the other hand, what color of skin and hair belonged to certain skeletal forms. That difficulty is caused by a fact easy to understand, by the mingling of different types among each other, and by the hybrid forms from which man is derived. It is true, however, that certain hybrid results seem to be limited to certain regions and to a few human groups; and that, on account of this, the elements which have furnished such products may be learned up to a certain point; but in the beginning, at least, it will be necessary to learn the structures of the parts from which hybrids are derived.

It is impossible not to admit human hybridism, since it is demonstrated clearly by all anthropologists; in this direction.

America alone shows us a perfect example of experimental anthropology. It is now determined from observations that human hybridism is multiform among all peoples; but what we learn from that example is the exchange of external characteristics and their mixture with those internal, that is, the union of the external characteristics of one ethnic type with the internal characteristics of another type. Thus, one may observe the color of the skin and hair with its special form united to characteristics of skeletons which do not generally belong to types of that color, and *vice versa*. That may be observed concerning certain characteristics, and not of all; such as the stature, or the face, with its soft covering, or the form of the cranium only.

If we study our European populations which are called white, but which have many gradations of whiteness, we may note the great mixture of characteristics, a mixture which is changeable, from which results a great variety of forms of individual types, constituted of characteristics differing from each other. An analysis must be very accurate and very minute to discriminate these different elements which exist in the composition of the ethnic characteristics of individuals and peoples. These mixtures and these combinations of characteristics differ according to the character and number of elements existing in the various nations of the south, the center, or the north of Europe. They arise from different relations with mixed peoples.

What is most important in this human hybridism, so various and so complex, is the lack of the blending of the external and internal characteristics from which new human varieties may be had. Among the different ethnic elements there exists only a relation of position, called syncretism, or propinquity of characteristics, and therefore a facility for forming small groups. Such a phenomenon has already been recognized in America, and it is evident in Europe among peoples who appear little homogeneous, if a careful observation separates the characteristics constituting ethnic types and those of individuals in a mixed population.

If there were no other cause for such an absence of blending among the characteristics of human hybridism, this cause would exist, that the relations which produce the mixtures are not equal and constant, but are varied and inconstant. If there should be the union of two pure ethnic types only, for several generations,

we should be able to derive a hybrid product constant and fixed, as among animals and plants; but a third element, either pure or mixed, arrives in the second or third generation of man, and so on indefinitely. Thus it is easy to understand how unstable must be the characteristics of the hybrid, for they can scarcely survive in one individual for a generation. The hybrids which follow may have characteristics of different types, with the tendency each time to have these reappear by heredity, although not blended and not fixed in the individual.

To this should be added another fact, that of individual variation, which is present in man, as in other animals, increased by his constant interminglings, which may be considered stimulants of this phenomenon, as has been suggested by Darwin and Wallace.

Hence, I conclude from my observations, that human hybridism is a syncretism of characteristics belonging to many varieties, and that these do not modify the skeletal forms as do individual variations, and that hybridism may affect different parts of the skeleton, constituting characteristics in themselves distinct. The stature, the thoracic form, the proportion of the long bones, may be united with external characteristics differing from each other, as well as from different cranial structures. The cranial form may be associated with different facial forms, and inversely. It happens, however, that the structures taken separately remain in part unvaried in the hybrid constitution. The face preserves its own characteristics in spite of the union of different cranial forms; so also the cranium preserves its structures, associating them with different facial forms. The stature preserves its own proportions in spite of its association with different cranial and facial types, and in spite of the different coloration of the skin and the form and color of the hair. All this may be affirmed, particularly of much larger human groups which, according to external characteristics, may be considered much nearer than they really are in geographical position, as the so-called white races in Europe, the negroes in Africa, in Melanesia, and so on.

Now, granting that all peoples exhibit the characteristics of hybridism in the manner just described, it will be necessary to learn how races, groups and human families may be classified. Let us observe for a moment the classification by means of external characteristics, most common among anthropologists from Linnaeus to Quatrefages and Flower, and we shall see:

1). That the color of the human skin in one great group of a type, such as yellow, black, or white, is of different gradations and not uniform.

2). Since, as above stated, all peoples, at least in a great measure, are composed of hybrid elements, it happens that different elements are united under one category, which is, in this instance, the color of the skin.

3). We must not forget that the external characteristics are more easily lost, and much easier to acquire, by intermixture and heredity.

A curious example of what I state is found in human classification according to Quatrefages, which perhaps is now the most complete, considered only as a classification by external characteristics. He places the Abyssinians within the white race notwithstanding that they have the negro coloring, and he does so because he believes that the characteristic form of the skeleton or internal characteristics of the Abyssinians are those of the white race. This is without doubt inconsistent when the principle of classification by color is accepted. This inconsistency itself shows the defect of the method and of the principles mentioned as applied to human characteristics and their combination.

4). Finally, as we perceive, the theory is not justified that man be classified as a single species with three, five or more variations.

If the characteristics which present greater stability are internal or skeletal, they should serve for human classification:

1st. Because, notwithstanding amalgamation and consequent hybridism, the characteristics originating in the skeleton are persistent.

2d. Because they may be taken as fixed points with which other characteristics may be associated, and may be also external, as I shall demonstrate.

3d. Because, finally, the internal characteristics can demonstrate the full number of divisions and subdivisions in classifying ethnic groups, and in analyzing peoples which are a combination of a great number of hybrids.

It remains to determine which internal characteristics should have the preference in deciding the value of types for classification. If we consider the human skeleton, with that object in view, we find three parts which may serve for that purpose, the cerebral cranium, the face, and the stature, with the long bones.



*Stature.*—The stature is a good, but an insufficient characteristic, because it gives only linear differences, and in its value resembles greatly other external characteristics, and is associated with all the most dissimilar derived from the skeleton.

*Face.*—The face offers very important characteristics for classification, because it shows typical differences in the ethnic groups. The face has given more points for the distinction of human types than the other parts of the human body, and would appear better adapted for that purpose than the cerebral cranium. But the face is more disposed to individual variations than any other part, because it is very complex, being composed of numerous small bones, clothed with muscles which have continuous and important functions relating to the physiognomy, to the expression of psychological conditions, and to the nutritive functions. These facts render its typical form less constant, and are, or may be, the cause of a multiplication of types.

*Cranium.*—The cerebral cranium is itself also liable to variations. More than any other organ, it exhibits a phenomenon often observed and clearly demonstrated by me, that is, the persistence of forms from immemorial epochs, and their reproduction through numerous generations notwithstanding amalgamation with other types. I have demonstrated such a persistence of cranial forms in the varieties of the Mediterranean from the Neolithic and from the most ancient Egyptian epochs; other anthropologists have recognized such persistence in European types of the Quaternary epoch, and in others, very ancient, from America. This cannot be said of the structure of the face.

Therefore if the human cranium is accepted as the basis for the classification of human groups, positive results may be had:

1st. In groups which have been subjected to mixture in whatever epoch or however many times, the distinctive ethnic elements may be discerned by examining the cerebral cranium only, which, remaining unaltered in type, may be found united by hybridism with other internal and external characteristics. For the cranium is the point about which revolve all other variations of form, either in hybridism or in the human form itself.

2d. Knowing the cranial types of a people who seem more or less homogeneous, we are sure of learning of what and how many ethnic elements it is composed, notwithstanding the hybridism present.

3d. Having classified all the cranial types in different regions and among different peoples, we may learn by their geographical distribution the numerical extension of types and also their geographical origin; that is, the place of departure and the course of emigration and dispersion of such forms.

4th. Then it will be easy to learn what cranial characteristics are found among populations which already have ethnic names, ancient and modern, and to discover among them points of similarity and difference.

Being, therefore, obliged on account of universal human hybridism to select as a guide to classification the most important and the most useful of the internal characteristics, we find greater advantages in choosing the human cranium, about which all the other characteristics, internal and external, are grouped. If we select one characteristic, or a number of variable characteristics, we shall find ourselves in the same position as other anthropologists who classify by external or accessory traits. It follows that accepting the cranium as the principal internal characteristic, we impliedly accept the brain in its various forms, and the brain is the most important of human organs.

## II.

The classification of man by means of the cranium alone is by no means new. It will be well to consider these schemes, from that of Retzius down to the last, that of Kollmann. Nor, indeed, is the conception of the importance and superiority of the cranium for distinguishing ethnic groups by any means recent. To show that, we have but to refer to the enormous work which has been done, from Morton to Davis and Thurman, from Broca to G. Retzius, to De Quatrefages, to von Holder, to Ecker, to His and Rutimeyer, to Virchow, to Ranke, to others still more numerous, in Italy, from Nicolucci to Mantegazza.

Notwithstanding so much labor expended on the human cranium, satisfactory results were not reached, nor, indeed, I may affirm, have we yet reached them, at least not in the signification which I intend these results to have. The fault lies in the nature of the method of studying the human cranium and in the value attributed to craniometry.

The classification of Retzius is based upon a single characteristic of the cranium, which, however, is merely the numerical expression of the *norma verticalis* of Blumenbach, that is, the cephalic index.

According to Retzius we have only two forms of crania, the long and short; though, in fact, many forms of short and long crania are found differing very much from each other.

When craniometry was developed in a systematic manner, following principally the work of Broca, it appeared the key of anthropology, and took the first place among means of investigations, as being the most effectual method for distinguishing human races. The French exaggerated its value; the Italians followed with zeal, in spite of the skepticism of Mantegazza, the head of the Florentine school of anthropology; the Germans have been more rational, and with them the Swiss, represented by His and Rutimeyer. At the head of them I would place Blumenbach, who based his small but valuable book upon a rational foundation.<sup>1</sup> The Germans try to establish cranial type almost or entirely independent of the cephalic index; as one may see from the works of von Holder, of Ecker, of His and Rutimeyer, of Virchow, of Kollmann, of Ranke and others. In my opinion the German method is an approximation to the truth, but unfortunately the conception of type is undeveloped and, I should say, has remained rudimental, because craniometry, like a pernicious weed among the grain, injures the harvest. Virchow, the most pronounced scholar in anthropology, and the man who has studied more than all others the crania of all peoples, believes that the germ of a sound anthropology should develop from it. He concedes only a secondary value to craniometry; but, nevertheless, in his last work, *precisely when he distinguishes types*, attempting to establish them definitely, he determines them by craniometry alone. In fact, in his great work, *Crania Ethnica Americana*, he defines types in this manner: "Die Form ist long, schmal und relativ hoch," or, "Die Form des Schädels ist hypsi-brachycephal," and gives the index and the measures. Now the reader who will observe that the Araucanians, the Pampeans, the Chilians of Huanilla and of Copiapo, and the Peruvians of Iquique, have the

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<sup>1</sup> *De generis humani varietate nativa*. IIIa edit. Göttingen, 1795.

hypsi-brachycephalic form of cranium, will not understand why the illustrious author constitutes of them different types, defining them always with the often-repeated proposition, "Die Form des Schädels ist hypsi-brachycephal." That the forms of such crania differ is evident from the fine lithographs, and not from the description, much less from the definition. Why has the celebrated anthropologist stopped on the way and has not developed the idea already promulgated by him and by his compatriots? I find in the *Crania Helvetica* and in the *Crania Germanica* of von Holder and of Ecker that the conception of type is more evident and has also a nomenclature, which is the only means of distinguishing typical forms.

According to my observations upon craniometry, which has now become cabalistic, especially in France, on account of the abuse of measures and numerical ciphers, the indices of the cranium and face are taken as a means of distinguishing races, human groups, as we might call them, and other measures are either omitted or applied only to individuals. In order to be convinced we should carefully and conscientiously study the craniometrical works of Dr. Danielli, of Florence, upon the Nias and Bengalese. The author has not been able to find satisfactory results after persevering researches, but whoever would seek evidence of individual variations will find more than enough. It seems to me, therefore, that the method by measurement may serve this purpose, that is, to discover numerically individual differences, but never those typical of a race. But such a discovery is useless, since we are all convinced of the existence of individual differences. I will therefore add that such differences, to be valuable, must be sought, not among forms differing from each other, but among individuals of the same type. That implies, therefore, necessarily and always, the search for types and their distinction, which is not possible by means of the craniometrical method.

Craniometry considers two forms, with a third of transition: the cranium long, and relatively narrow; the cranium wide, and relatively short, that is, dolicho- and brachycephalic, the form between which is mesocephalic. These forms, as I have said, are expressions of the normal line of Blumenbach, but imperfect, inexact and insufficient, as a brief demonstration will show.

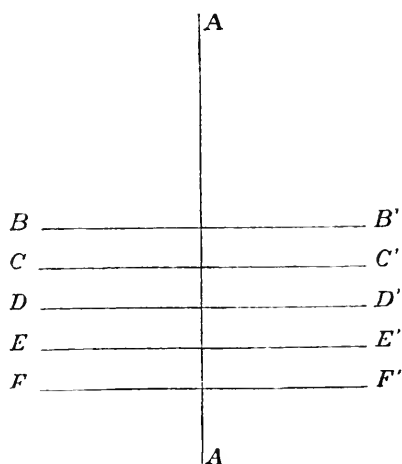


FIG. 1.

Let  $AA'$  be the antero-posterior diameter of a cranium,  $BB'$  the greatest transverse; it is evident that, given the norma verticalis with such diameters and with the greatest transverse at the conjunction of the line  $BB'$ , this norma verticalis takes a particular form on account of the curves which surround the two diameters. This line or curve, which surrounds them, is called  $X$ . If the greatest transverse is placed back and is made to coincide with the line  $CC'$ , the curve will be modified and will no longer be  $X$  but  $Y$ . That will be equally true if the transverse diameter is placed still further back at  $DD'$ ,  $EE'$ ,  $FF'$ ; then we shall have a third curve  $Z$ , a fourth, a fifth,  $n$ , that is, we shall have as many different vertical curves on account of the changing of the diameter of the width, as the index causes; that is, the relation between the length and the width will be the same.

From this it may be judged how much more will the norma verticalis vary if the form of the curve circumscribing the two diameters be modified in other ways, that is, by the frontal width, by the occipital form, and so on. If we also add the lateral curves, those posterior and anterior, which serve to show the form of this irregular body, we shall easily be convinced that the cephalic and vertical index cannot give the cranial form. That is why I have above stated that the expression of Virchow, "The form of the

cranium is hypsi-brachycephalic," is insufficient to define the form. While cranial types so defined have equal indices, their curves differ in degree, and therefore the skull may or not be hypsi-brachycephalic. It is just as if we attempt to calculate the size of an ellipsis by means of the relation of its two axes. Two ellipses equal in this relation may be unequal in size, and this is why these two relations cannot be compared. It is the same in regard to the cephalic and vertical indices of the cranium.

If it were true and there were no doubt respecting the value of the celebrated cephalic index in determining cranial forms, it would follow that all human crania of whatever type and volume should be placed in the three categories of dolicho-, meso-, and brachycephalic, or of hypsi-, ortho-, and chamaecephalic. Thus all the populations of the earth, either of white, yellow, black or red skin, would have crania belonging to the three categories. A classification solely according to the cephalic index is therefore an absurdity. It is incoherent and without meaning, as are those of Retzius and Kollmann.

This conclusion is so true that such anthropologists are obliged to add descriptions to the forms of each part of the cranium, in order to distinguish it, recognizing the insufficiency of cranial data. Such descriptions can, to a certain degree only, supply the defect of the method, but they always remain incomplete, and leave the forms or types of the human cranium of various populations and regions indefinite. The French school has gone still farther and has supplied the deficiency with an infinite number of measurements, which only increase the obscurity, leaving the conception of the form more uncertain, and fatiguing the most patient student, who becomes convinced of never reaching any satisfactory result from such a confused accumulation of numbers.

In order to render classification more definite, or for the sake of finding a second characteristic which might be associated with the cephalic index, Retzius turned his attention to the prognathism and the orthognathism of the molar teeth; Kollmann to the facial index. Use could be made of the nasal index instead of the facial, or the orbital index, or any isolated characteristic, and we should have the same results. The combinations given by Retzius and Kollmann are possible, but cannot indicate races or varieties, from the fact that they are hybrid associations.

I need not make a longer demonstration of what I have affirmed, that classifications of human groups have been attempted by means of the cerebral cranium, but have not been successful on account of deficiency of method; and that the craniometrical method, still so undeveloped, has not yet, nor cannot, give those results while there is an exaggeration of an exact principle, that of expressing numerically facts relating to the cranium. It seems to me, after several years of study, and after having adopted the accepted form of craniometry, for want of a better, that it is time to establish for our use and for the study of the variations of man, a natural method, resembling that which is used in zoology and botany, and of which I laid the foundation about two years ago.

### III.

The human cranium presents two kinds of variations: the first are those which change their general form and present types differing from each other; the second are those which do not change their typical form. The first have stable characteristics, therefore hereditary, and which passing through many generations remain unaltered and persistent; the second are the variations of the individuals of a type, and, of course, being transitory, do not in any way alter the typical forms; they are the so-called "individual" variations.

There is no need of recapitulating the facts which relate to variations in the human cranium, nor of seeking their causes, since the investigations of Darwin, Wallace and others concerning the variability of organisms, well known to all students of biology. I would simply state that the various phenomena of variation are repeated in man, and, for the case in point, in the human cranium.

The relation which exists between the two kinds of variations is close, and it is possible to admit that individual variations have given origin to permanent variations, just as it is easy to accept the idea that the process of variation in animals and in man in the cranium and the brain is continuous and constant. However that may be, an observer accustomed to large and small series of human heads perceives immediately that such series may be divided into groups, different and distinct, according to the form



of the cranium itself, and that some difference, often difficult to describe or explain, exists among the elements of the groups; and this difference is derived precisely from the individual variations of the groups themselves. While the character of individual variations is transitory, the character of those which give typical forms is permanent; their persistence consists in being hereditary and numerous in each generation.

We know that the so-called "species" of the animal kingdom have forms derived from some variations of characteristics, and that they are such because the variations from the mother-species are permanent and become transmitted by heredity. These forms may be called "varieties" of the "species," or races, according to some, or subspecies, according to others. We will call them "varieties," because the name indicates their immediate origin. According to Darwin, a variety is a species in the process of formation, because it still bears many characteristics of the species from which it is derived, and cannot become an independent form, like the species itself, until it acquires still more diverging characteristics.

If we apply this principle to the human cranium, we should first learn if man comprises a single species, as many anthropologists believe, or has many species. In the first case, the typical variations of the cranium would certainly be varieties; if, however, there are several human species, the problem becomes more complicated. In that case the varieties might be of one species, and a primitive type be found to which it is allied. But if of such primitive types there were several, these would form several species which should be grouped under one genus.

I cannot venture the solution of the general question regarding the unity or plurality of the human species, considering the actual state of my personal observations, limited to Southern Europe, especially the Mediterranean, to Oriental Europe, and to the Kourgans of Russia. I should examine Asia, Africa, Oceanica, America, Central and Northern Europe, before being able to give an opinion on such a problem. I will call therefore varieties only, human varieties, the typical forms of the cranium which are clearly distinguished from each other by their own and diverging characteristics, while I will suppose that such varieties may converge in different species, of which I cannot now give the type

nor characteristics. Meanwhile it is useful to know and describe the "varieties" under this name, with the purpose of learning their distribution in the various regions of the earth.

With the present uncertainty about human varieties, I could have no intention of publishing a work which would treat of general theories, nor would I have thought of the present pamphlet had not necessity demanded it. This essay is only designed to give direction to the method of research, because many students have requested it, and in order to place before the public ideas and facts which others either misunderstand or condemn without knowing them.

Calling the typical forms of the cranium "varieties," we have the advantage of finding the differences or individual variations of the same type, and also certain differences which cannot be reduced to individual variations, but which are equally repeated as diverging characteristics of the same variety: these constitute subordinate groups or "subvarieties." The "subvariety" therefore diverges from the "variety" by a new characteristic which it retains in a persistent manner. We have an easy means of recognizing varieties and subvarieties, and of distinguishing them from individual variations. The latter are not repeated, or if there is repetition it is accidental; varieties are repeated by groups more or less large, which, in addition, have individual variations; the subvarieties also repeat in lesser groups that characteristic or those characteristics of the variety from which they are derived.

One of the difficulties of craniologists is how to find the limits of individual variations, how to distinguish them from typical forms, or to admit that all cranial variations may be individual, especially if one population is studied without reflecting that any population is invariably a composition of many varieties, notwithstanding the misleading appearance of the external form and the exterior characteristics. We can clearly and easily distinguish by my method the individual variations from the true and constant varieties and from the subvarieties, and we can make a complete analysis of populations, as I have had numerous occasions to demonstrate.

Another prejudice of anthropologists is that human varieties, determined by my method, may be too numerous. The scientist cannot, indeed, free himself of certain sentiments which are

acquired in following scientific habits and which have become a part of science and public opinion, because in face of the danger of seeing human varieties doubled or decupled, he feels an aversion, like an instinct of preservation for that which is established and which has become the belief of most scientists and cultivated men. The human races until now have been either three, four or five, but never six; the first time it is affirmed that they may be twenty, opposition is inevitable; it is the *misoneism* of Lombroso, the inertia of the mind, which opposes such resistance, just as matter is opposed to every change in the direction of its forces. Treating of man, into which we ourselves enter with our sentiments, the opposition is greater, even in spite of good intentions. Notwithstanding this psychological phenomenon which influences us all, the force of facts is superior to every inertia and sooner or later will conquer.

With the observations and the methods which I propose, I believe that many errors will be eliminated from anthropology. Those errors have been accepted because we have never possessed natural scientific methods for the study of human classification, such as we have in zoology. To apply zoological methods to man appeared to lower him to his congenerous beings; and, while in zoology, science advances freely, in anthropology, on the other hand, preoccupations embarrass researches. I observe that such preoccupations do not exist in two very eminent anthropologists, although the contrary at first appears evident in one of them—Blumenbach and De Quatrefages—at least a century apart. Blumenbach, in a valuable little book, attempts to apply the zoological method to man, not only for classification, but for the explanation of the causes of animal and human varieties. De Quatrefages, in his last work, employs the same method and the same scientific freedom. Unfortunately the followers or successors of both have only followed their masters in form, but not in method. Blumenbach, who, after various researches, reduces the human species to five varieties, finds, however, that human variations are infinite in number. If his method had been followed strictly, the number of human varieties would long ago have been increased, both in respect to the structure and the cranial forms.

The neglect of such methods and the failure to distinguish human varieties by means of the cranium has caused a curious

error, that of regarding certain forms which are typically normal, as pathological, as I shall have occasion to demonstrate in the future when I speak of classified forms. This is apt to happen when new and unrecognized forms are placed before the observer.

One of the important characteristics in classifying the cranial varieties of man is the *cranial capacity*, which has a direct relation to the volume and weight of the brain; hence classification by crania means the classification of brains estimated by their form and external configuration. Its importance is for us increased by the fact that that which we find among races of animals occurs also in man; that there are races of small and large animals, races differing in size. This is also repeated in man, and we therefore have large, medium and small varieties, as measured by stature. The origin of such varieties is perfectly analogous to that in other animals. Nor is it an accidental phenomenon, because it is confirmed by heredity, through numerous and indefinite generations.

I have concluded, in studying cranial varieties morphologically as human varieties, that is, by their characteristic structures, that the volume has a direct relation to the form, that is, many forms have limited and definite capacities, while other forms have sub-varieties differing in capacity. Such varieties are analogous to the stature of the large and small varieties of animals. The cranial capacity, therefore, while it is one of the integral characteristics of the cranium in regard to its classification, is also the indication of different varieties according to size. I discovered this fact when I classified for the first time the crania of Melanesia, and subsequently I defined it more accurately when I examined and classified thousands of other human crania.

This fact points to a correction of the value of cranial capacity and therefore of the weight of the brain, until now calculated by the average without distinction among different varieties. The cranial capacity of man varies from 1000 cc. to about 2000 cc. in the masculine sex; this enormous difference is admitted as individual variation, and it is thus conceded that there may be a least limit of normality possible which can be ascribed to the function of the brain, crania which descend to 1150 cc. being considered as pathological microcephali, according to Broca, and more or less according to other anthropologists; giving, on the other hand, a great value to a large capacity. Both conclusions are contrary to

the real significance of the facts. I have found normal masculine capacities of 1000 cc. and a little greater, representing small human varieties, not being sporadic and individual phenomena; and, on the other hand, anthropologists have registered for eminent men like Dante, Gauss and others, very mediocre capacities, even very low, while for ordinary men they have recorded a much higher capacity. I have found in Melanesia normally constituted heads absolutely microcephalic, together with megalcephalic heads, belonging to varieties which have the same social value; they are both inferior, some anthropophagous, and live mixed together as one people. That which I have asserted concerning Melanesia may be said of the ancient and modern populations of the Mediterranean, among which are the Sicilians, the Sardinians, and the inhabitants of Central and Southern Italy; and I do not believe it can be said that there are no signs of human superiority in those regions. There are not, therefore, individual differences so great as from 1000 to 1500 cc., and from 1500 to 2000 cc., but characteristic differences of variety in human forms. The general average I therefore maintain is inexact and still further arbitrary, because it is the average of incommensurate quantities. The exact average is that between individuals of the same variety, and the difference is the true individual variation.

But there is another error to correct due to the signification which I am able to give to varieties distinguished by means of my method. It is considered by some a demonstrated fact that the cranial capacity has been increased in the course of social evolution from prehistoric epochs to historic times. Eminent men have affirmed it, but I have already placed their conclusions in doubt, because the facts do not appear to me evident and affirmative. I wrote some years ago:<sup>1</sup> "The most important physical evolution of man would be that which related to the organ of the mental functions, the brain. But the facts are still very doubtful and very obscure which relate to the weight and volume of the brain, and consequently to the cranial capacity. In a recent work of Professor Schmidt I find that the cranial capacity of the ancient pure Egyptians is 1394 cc. in the masculine and 1257 in the feminine sex; in the pure modern Egyptians it is 1421 in the males, 1206 in

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<sup>1</sup> *Human Evolution*. Review of Scientific Philosophy, 1888, Milan.

the females. According to these figures there would be an increase of the cranial capacity of the modern over the ancient males, but a decrease in the females. The reverse would be true of the Egypto-Nubian cranium, which is 1335 in the modern males and 1205.8 in the females. Broca found that the Egyptians of the IV. Dynasty had, males 1534, females 1397 cc.; those of the XI., males 1443, females 1328; and, finally, those of the XXIII., the most recent, males 1464, females 1322. There would be in such a case no increase, but decrease, but that is not possible; the cause of these facts lies in the mixtures of races at different times and in different proportions."

Now I conclude from my recent studies upon the Egyptians of different dynasties, from the most ancient to the present, that according to my method of classification there are capacities of 1260 cc., of 1390, of 1480, of 1550, of 1710, and still other capacities differing according to the varieties determined.<sup>1</sup> As is easily understood, a general average necessarily alters the facts, according to the number of varieties which enter as components of the average in the different series in anthropological museums; hence the curious results above indicated.

Another important point is as follows:

"But the fact which surprises us is the high figure of the capacity given by prehistoric crania. The masculine crania of Lozère have given 1606 cc., the feminine 1507; also of Lozère, masculine 1578, feminine 1473; crania from the *pietra levigata*, masculine 1531, feminine 1320; the contemporaneous Parisians, masculine 1550, feminine 1337. The approximate average of crania from the *pietra levigata* is 1560, equal to that of modern Europeans, as is related by Topinard."<sup>2</sup>

In another of my recent works I have demonstrated that of the crania of the neolithic age<sup>3</sup> the *Isobathypatycephalus* has a capacity from 1230 to 1405 in the feminine, and the *Eucampylos* varies from 1470 to 1564 in the masculine. The two varieties, still persistent in Sicily, do not vary in capacity in the modern series, and at the same time show that in the neolithic epochs, as among

<sup>1</sup> Concerning the Primitive Inhabitants of the Mediterranean, Archives of Anthropology, Florence, 1892, Vol. XXII.

<sup>2</sup> See *Human Evolution*.

<sup>3</sup> *Crania of the Neolithic Age*, Boll. Paletnol. Italiana, Parma, 1892.

modern populations, large and small varieties are found, just as the same types are now found through persistence of forms.

From this it is evident how much there is to reform in anthropology when we study by natural methods facts until the present misinterpreted, respecting the classification as well as the physical and psychological characteristics of man in time and space. Perhaps in the future, when we know all cranial forms by natural classification, it will be possible to find a correspondence of psychological characteristics in populations according to the predominance or superiority of types, a fact which has until now escaped research, because the capacity of the cranium in its absolute sense is not in correlation to the development of the mental functions, notwithstanding what is commonly affirmed. The reform is urgent, but a natural method should be employed, and that is my purpose.

## PART SECOND.—METHOD AND CLASSIFICATION.

### I.

#### *Varieties.*

The greatest variation in a series of human crania cannot be distinguished by an untrained eye; anatomists continually accustomed to the study of the human skeleton and scholastic demonstrations do not at first discover the salient points of difference among crania, their attention being distracted by observing the single parts of which they are composed, the canals, depressions and minor details, and does not grasp the complex form of the entire cranium. There are two different kinds of observations: one is useful in examining the development and normal condition of the cranium; the other serves for the classification of forms, and it is this last method of inquiry which I am about to consider.

The distinctions of forms depend in the first place on the comparison of different crania. They should be placed upon a table and compared in every direction. Little by little a useful habit and keen eye are acquired, by means of which the slightest variations are detected, so that the similarity of fundamental characteristics can be seen among great differences which at first appear absolutely dissimilar.

The practical method which I have already adopted, for me and others who wish to make use of it, is that of placing the series of crania in order and in an equal row upon a large table, the first time, if possible, of the same color, intact, that is, without having been sawed to extract the brain, without the lower jaw, and therefore upon a single plane, each placed upon its base. Difference of color, the line which divides a cranium sawed, an inequality in the table, may alter the positions of the forms or render the discovery of similarities and differences more difficult.

When familiarity with the forms has once been acquired, many of the conditions become superfluous, and then an isolated cranium is classified without the necessity of a comparison, at least in the forms which are common.

After various and attentive observations and continuous comparisons, it is necessary to form groups of crania which seem to have common characteristics. Formed in groups, each group must be separately analyzed in every component, in order to recognize common and diverging characteristics; if these last are marked, separate the groups into subgroups, noting the individual differences which must necessarily exist.

Formed in groups and subgroups, one typical cranium is selected for each group or subgroup, and its likeness is transferred by drawing a free-hand outline, by placing the cranium itself upon paper, or by means of a camera, and finally the volume is reduced, or rather the linear magnitude, to a third or half, making this reduction equal in all the crania which are designed. Drawing has the very great advantage of revealing the linear curves, which are not immediately observed, and demonstrates characteristic differences very easily. In case of doubt concerning certain forms which seem similar, it is well to place the profiles one above another, in order readily to observe similarities and differences, whether apparent or real, profound or superficial.

The following are additional rules: Distinguish the crania which compose the groups according to sex, because sexual differences should not impair or alter the types under which the crania are classed, nor should another type be made on account of characteristics which are merely sexual. The observer should be trained to discover the sexes of crania and sexual characteristics distinctly and clearly. When the groups are formed, the crania



should be adult, though when special conditions permit, those of infants can be added. We should bear in mind that the forms of the latter are never decided, just as they are not permanent. The condition of the sutures and of normal or abnormal development should be taken into account, because abnormal development, as well as the partial arrest of development, may profoundly alter typical forms; exclude, therefore, all pathological crania when this pathological condition is apparent. I have, however, been able to observe and will demonstrate in a future work<sup>1</sup> that crania belonging to persons of enfeebled mind, in spite of various alterations, preserve the typical forms and are recognizable without difficulty by those experienced in the method and classes of forms.

The examination of the cranium must begin with the well-known *norma verticalis* of Blumenbach, that *norma* from which, in turn, Retzius derives the index of the width. It should furnish us the first form or the first characteristic for classification. When the vertical line is undecided, or cannot be reduced to a normal form, then the *norma lateralis* must be observed in order to ascertain the first characteristic; it may also happen that the lateral modifies the *norma verticalis* so profoundly that it may be preferred to this, or that it may have a characteristic much more prominent and more easily distinguished than the vertical; in such a case it should have the first place. It may also happen that another characteristic may be more decided and more marked, giving it the preference, and such a characteristic may be visible in the *norma occipitalis* or *norma facialis*; this should then be selected as the first characteristic for distinguishing varieties.

Let us now consider those characteristics which should separate and classify varieties according to the natural method. I begin with the forms given by the *norma verticalis*, as they are those which are easily distinguished and can be in great part reduced to geometrical figures.

1st. ELLIPSOID (*ellipsoides*) (Fig. 2).

We will call *ellipsoid* a cranium which in the *norma verticalis* presents an elliptical contour, as in the figure reproduced, taken from life, and which I insert in the parallelogram in order to show

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<sup>1</sup> This is the work of Dr. G. Mingazzini, entitled *Concerning the Craniology of the Insane*.

its regularity and demonstrate how the exterior outline harmonizes with the lines which surround it. Ellipsoid, or whatever similar name is adopted, signifies a body which has an outline similar to an ellipsis. Such an elliptical form, very common among varieties of crania, necessarily has all the projections rounded off, the occipital is never flat, and the parietal protuberances are always slight, or do not exist; the transverse curve of the norma verticalis or cranial arch is moderately or decidedly convex.

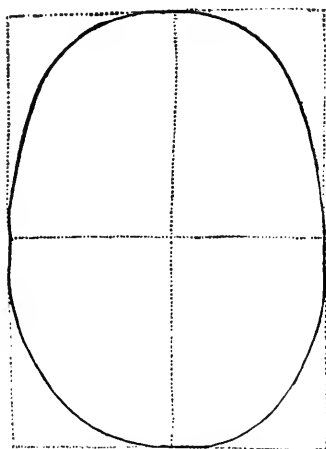


FIG. 2.—ELLIPSOIDES.

A form of this kind, considered only as norma verticalis, is subject to variations in length and width; hence it may be a short and wide ellipsis, *brachyellipsoid* (*brachyellipsoides*), a long one or a narrow one, *dolichellipsoid* or *stenellipsoid*.

2d. PENTAGONOID (*pentagonoides*) (Fig. 3).

Figure 3 shows a pentagon of unequal sides, but symmetrical, into which is inserted a cranial form corresponding to its respective sides, but with rounded angles, of which the most rounded, which is cut off, is that which corresponds to the occipital cone. In this cranial type the parietal protuberances are pointed, and often with corners definite and acute; from these points towards the frontal there is a gradual narrowing, and so also towards the occipital; but with this difference, that while from the parietal

protuberances forward this narrowing, which forms the two symmetrical sides, is maintained almost at the same level as the cranial arch, the level from the parietal protuberances to the occiput becomes oblique and descends to form the angle of the pentagon.

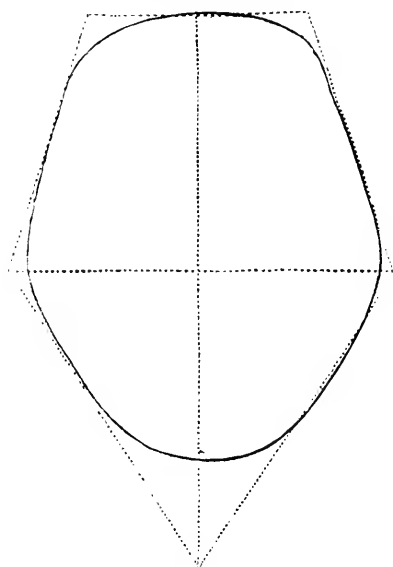


FIG. 3.—PENTAGONOIDES.

This obliquity is very evident when seen from the norma verticalis (Fig. 4).

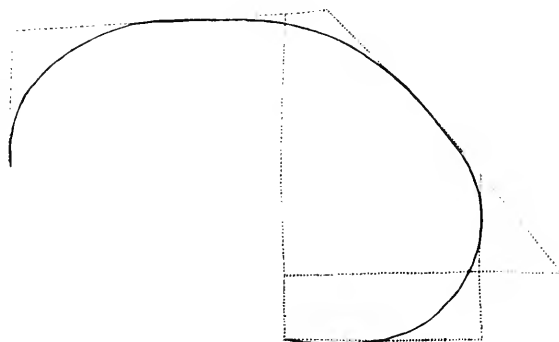


FIG. 4.—PENTAGONOIDES.

The variations which the pentagonal norma verticalis may present are as follows:

1st. The corners are acute or obtuse; whence a *pentagonoides acutus* and *obtusus*: the anterior part of the cranium, that is, the two sides which reunite the parietal to the frontal protuberances, can be longer or shorter than usual; there will then be a *pentagonoides oblongus* or a *brachypentagonoides*.

3d. RHOMBOID (*rhomboides*).

The rhomboidal form of the norma verticalis (Fig. 5) can interchange with the pentagonal form, because the most characteristic difference consists in the suppression of the one side corresponding to the frontal width.

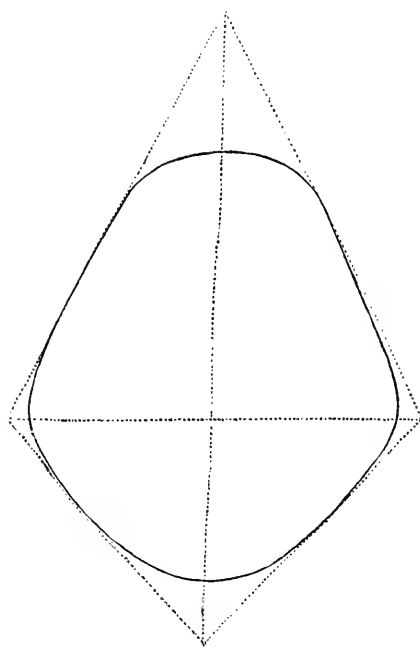


FIG. 5.—RHOMBOIDES.

This side is very short in the rhomboidal figure of the cranium when considered in relation to the biparietal width of which the protuberances are very distinct and pointed; so the occipital projection is still more acute on account of the greater convergence of the two posterior sides. In this variety the cranium is smooth in the sagittal line, low in relation to its width and length.

Of this singular form I have so far found two variations distinguishable by the norma verticalis: 1st, the *australensis*, of which I give the type in Fig. 5; and 2d, the *brachyrhomboides aegyptiacus*, shorter and wider than the preceding.

N. B. That these forms are often found in infantile crania is a fact worthy of attention.

4th. OVOID (*ovoides*). This form (Fig. 6) is distinguishable only by the norma verticalis. The enlargement of the cranium is at the parietals at about a third of their entire length and posteriorly. The occiput terminates at the large apex of the egg, while the second apex is represented by the frontal. The cranium has symmetrical curves; the arch is not always very convex and may have a transverse curve, slight and easy.

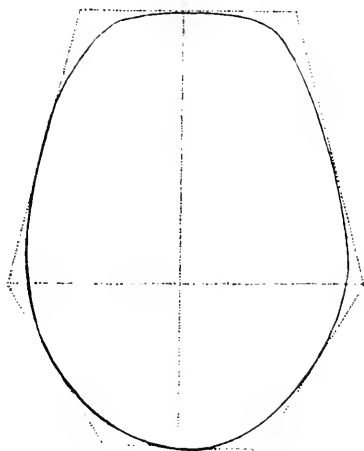


FIG. 6.—OVOIDES.

The ovoid cannot be confused with the pentagonoid, because it has no sides, nor apparent corners, nor has it the occipital obliquity which forms the posterior part of the two posterior sides of the pentagonoid.

The "Sardinian ovoid," which I have described and named *sardiniensis*, diverges a little from this type; the enlargement of the parietals is situated a little in advance of that in the type described, and, besides, the ovoidal appearance is also perceived in the norma lateralis.

5th. SPHENOID (*sphenoides*).

The cranium represented in Fig. 7, which I name "sphenoid," from the Greek, is cuneiform. The characteristics of this type are

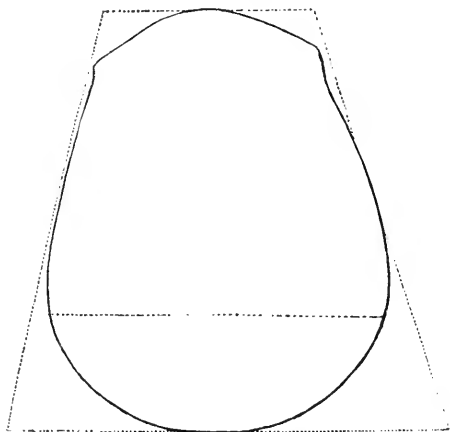


FIG. 7.—SPHENOIDES.

very evident; the biparietal enlargement of the cranium is far back, and there is a gradual and sensible reduction in width from that

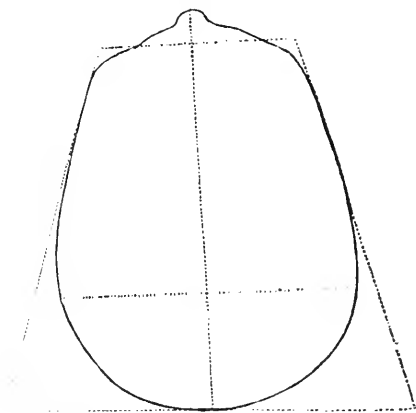


FIG. 8.—SPHENOIDES STENOMETROPUS.

unusually large extension as far as the frontal. The occipital part is, therefore, either level and vertical, or rounded, without protuberance.

This form, seen in the *norma verticalis* only, is subject to many variations, preserving, however, the characteristics which clearly distinguish it from others. I add some of the most common forms which I have found and classified.

1. *Sphenoides stenometropus*, that with a narrow forehead and generally a small capacity. This type is very common in the Mediterranean (Fig. 8).

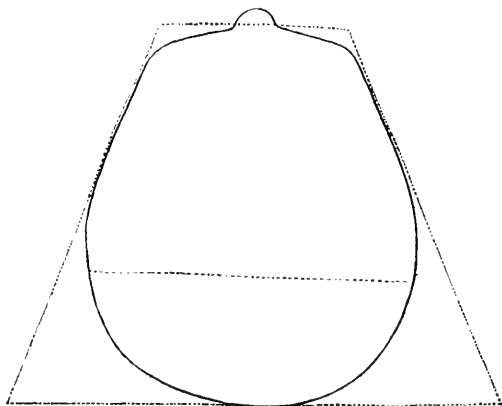


FIG. 9.—SPHENOIDES ROTUNDUS.

2. *Sphenoides rotundus* (Fig. 9), which is larger and wider than

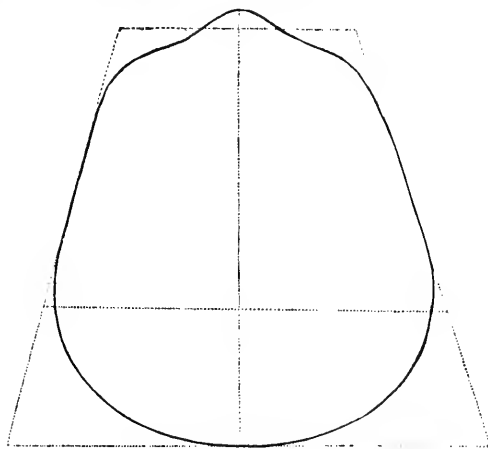


FIG. 10.—SPHENOIDES LATUS.

the former, and has the elevations rounded off, especially in the occipital part, which is globular.

3. *Sphenoides latus* (Fig. 10). This is much wider in its biparietal expansion and is short. It has the occipital smooth and per-

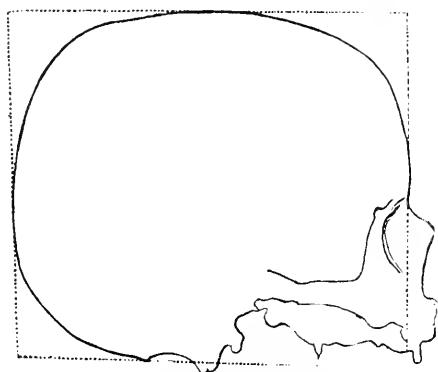


FIG. 11.—SPHENOIDES LATUS.

pendicular, the parietal prominences acute, the corners evident and the sides flat; observed laterally, this type appears cuboid (Fig. 11).

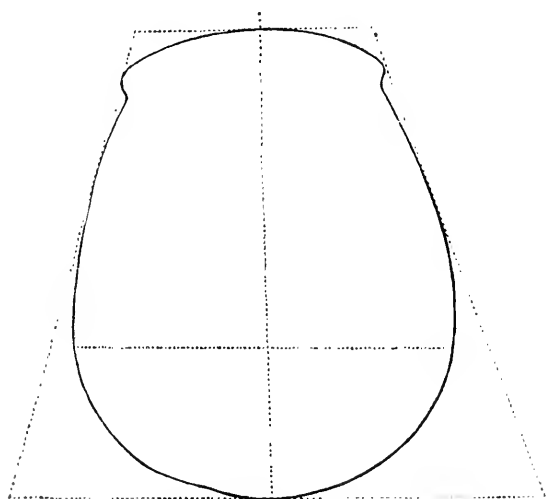


FIG. 12.—SPHENOIDES MEGAS.

This is the characteristic type of the Kourgans of Russia, and for that reason I have called it *kurganicus*.



4. *Sphenoides megas* (Fig. 12), the largest which I have found. It is also distinguished in the *norma verticalis* by a certain convexity in the sides of the cranium and by the posterior rotundity. This type is also obtained from the Kourgangs.

5. *Sphenoides oblongus*. I so name that sphenoid which has a marked distance between the greatest biparietal width and the bifrontal line. This type is opposed to the *latus*, which is short.

#### 6th. SPHEROID (*sphaeroides*).

The general character of this cranial form is the rounding of the frontal, parietal, parieto-occipital and the inferior or basal parts of the occiput itself, by spherical curves.

The cranium is relatively wide and short, the forehead and frontal large, the cranial arch widely convex, the occiput without protuberance, but rounding, the base wide (Fig. 13).

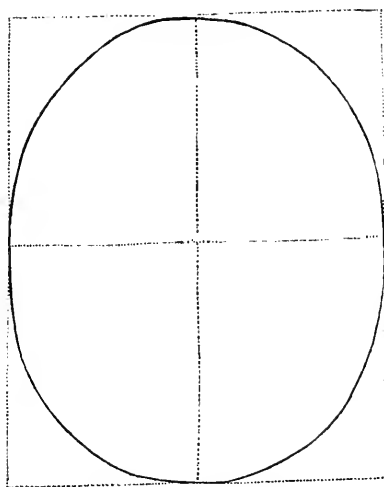


FIG. 13.—SPHAEROIDES.

I have already distinguished three principal forms of the spheroid, visible from the *norma verticalis*.

1st. *Sphaeroides* proper, which we also find subdivided.

2d. *Sphaerotocephalus*, which diverges by having a forehead wider but slightly retreating, following, therefore, the spheroidal

as far as the coronal curve, and which as a whole becomes less even in its curves than the typical spheroid proper.

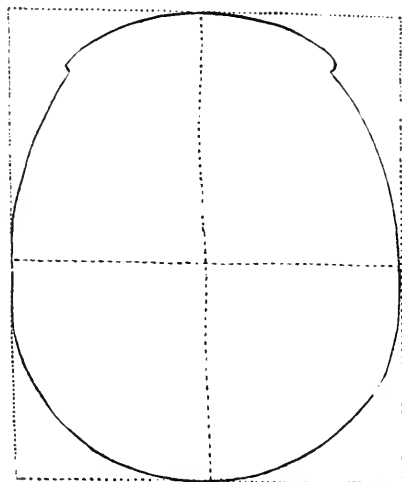


FIG. 14.—STRONGYLOCEPHALUS.

3d. *Strongylocephalus*. This type differs in that it has a narrowing in its sphenoidal fossae, visible in Fig. 14, so that the spherical part of the cranium is that which remains back of this narrowing.

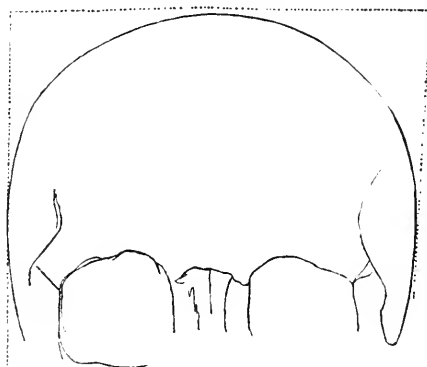


FIG. 15.—STRONGYLOCEPHALUS.

Fig. 15 shows also very well the frontal narrowing in its temporal lines, while the transversal curve is clearly spheroidal.

7th. BIRSOID (*byrsoides*) (Fig. 16).

The apparent form of this cranial type is an ovoid, which is removed from the usual form, because it has a rather large biparietal expansion, which does not terminate at the apex of the egg, but is rounded off; moreover, the curves, which are directed from the larger to the frontal expansion, are concave, with dilatation of the frontal line. Thus this form seems to be that of an elongated purse, the opening of which is found at the bifrontal line and the bottom at the expansion of the parietal curves, whence the name of *byrsoides* (like a purse).

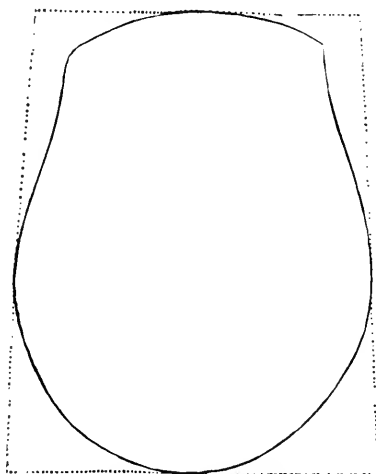


FIG. 16.—BYRSOIDES.

Observed from the side, the birsoid presents a superior plane; it is low, with the occipital rounding, but protuberant.

In its *norma verticalis* I have observed a variation among the birsoids of ancient Egypt; one with a smaller biparietal expansion. The cranium of this variety is large.

The seven forms which have been described are recognizable by the *norma verticalis*. The following are those in which the vertical is insufficient, uncertain or can be easily confounded with others which are different. Among these the following are found:

8th. PARALLELEPIPEDOID (*parallelepipedoides*).

Figures 17 and 19 represent a Sardinian type. The normal line has a slight swelling in the posterior part, and does not give the exact image of the form with parallel lines, while the lateral line corresponds to its name more closely. This form has a flat

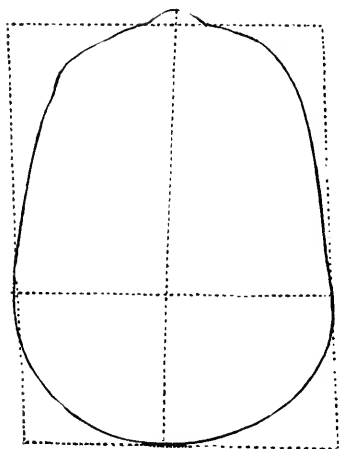


FIG. 17.—PARALLELEPIPEDOIDES  
SARDIN.

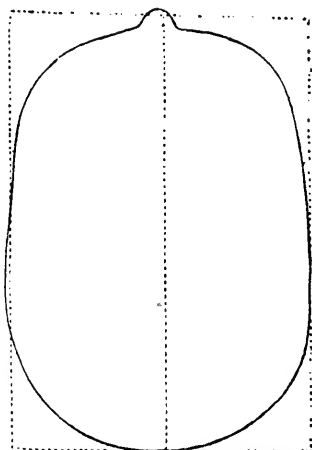


FIG. 18.—PARALLELEPIPEDOIDES  
KURGANICUS.

arch, vertical forehead, smooth occiput, and the base leveled; it is narrow, long, low, with smooth sides and evident corners, which makes a geometrical form.

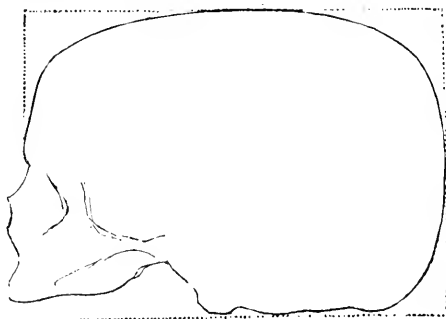


FIG. 19.—PARALLELEPIPEDOIDES SARDIN.

Figure 18 represents a *parallelepipedoid* from the Russian Kourgans. It appears very clear by the parallel lines of the two sides, its length and regularity.

This form is not very common, and can undergo variations in the *norma verticalis*, that is, can be larger in the transverse diameter, and hence relatively shorter; it is always low in the *norma lateralis* and through its entire length.

9th. CYLINDROID (*cylindroides*).

If the rounding of the corners and the sides of the parallelepipedoid renders it more convex, there is the "cylindroid," which is long, narrow, low, like the first, but rounded all around. Therefore the forehead is lower, retreating (Fig. 20), and, seen from the vertical, the occiput is narrow (Fig. 21); this occurs in the types here given, of which one (Fig. 21) is from Latium, the other from the Russian Kourgans. Such a form is rather rare, as is also the parallelepipedoid.

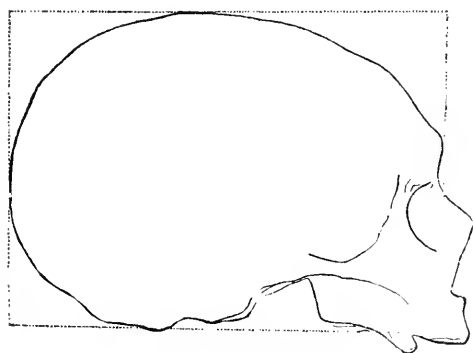


FIG. 20.—CYLINDROIDES.

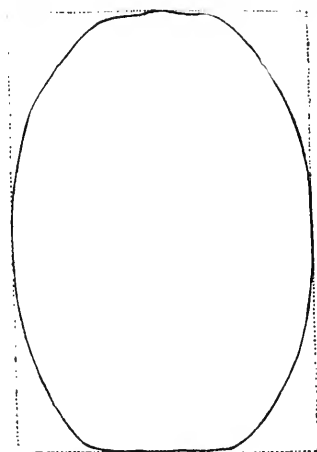


FIG. 21.—CYLINDROIDES.

10th. CUBOID (*cuboides*).

The cranium resembling a cube, has the arch, the occipital, and the sides smooth, and possibly the forehead, which is almost always vertical, at least in the small cuboids. One cubical form, which approaches nearer to its typical name, has the vertical line about corresponding to a quadrilateral, a little elongated; but we know that the anterior is always narrower than the posterior part of the cranium. As a rule, such a cranial form is more visible

from the norma verticalis (Fig. 22) and from the posterior (Fig. 23). The characteristic of the norma occipitalis is especially that the height is almost always equal to the width; hence we obtain the true cubical form from the side, this presenting a superficies of the cube.

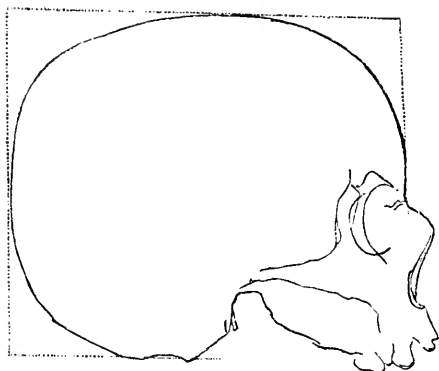


FIG. 22.—CUBOIDES PARVUS.

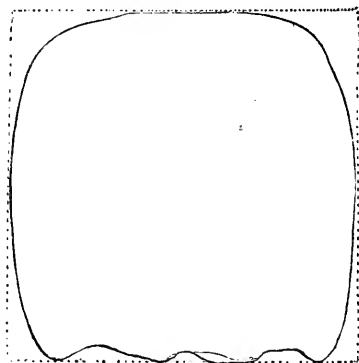


FIG. 23.—CUBOIDES PARVUS.

Figure 24 represents a *cuboides magnus* (from the Kourgans), while Figs. 22 and 23 reproduce a *cuboides parvus* of Sardinia.

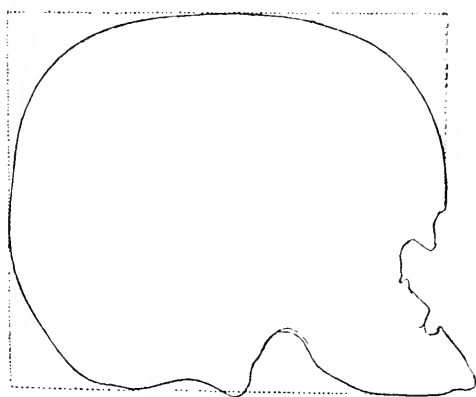


FIG. 24.—CUBOIDES MAGNUS.

Masculine cuboids may be found, especially large ones, with retreating foreheads and frontal sinuses large, and differing from the type Fig. 24.

The forms which follow are determined especially by the norma lateralis; first of all is the

11th. TRAPEZOID (*trapezoides*).

The two parallel sides of the trapezium here correspond to the

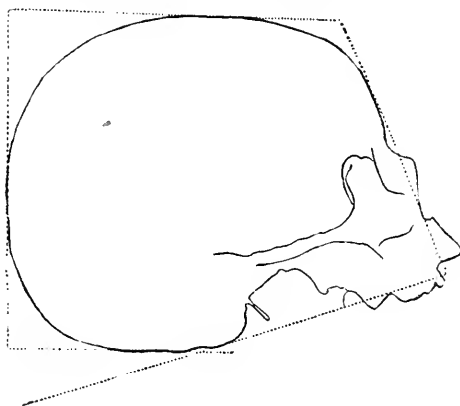


FIG. 25.—TRAPEZOIDES SARDINIENSIS.

arch and the base of the cranium (Fig. 25), the two sides not parallel are the sloping of the forehead, and the occiput more or

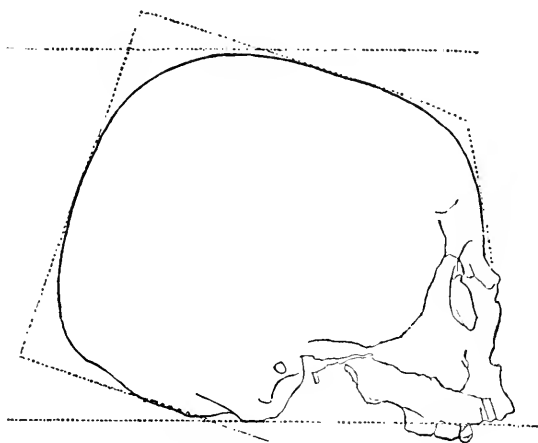


FIG. 26.—TRAPEZOIDES AFRICUS.

less oblique. The type which I show is the *trapezoides sardinien-  
sis*, a small microcephalous cranium. One important variation  
of the trapezoid is that which I have called African (*africus*),

which I have obtained from Harar, and which I have seen again in Russia, especially in the Government of the Chersonesus.

The Sardinian type is distinguished by being higher in the back, wider in the *norma verticalis*, and relatively short (Fig. 26).

In order to recognize this form it is necessary to know that the greater height of the cranium is at the back, and thence there is a perceptible sloping towards the forehead, which is low. The

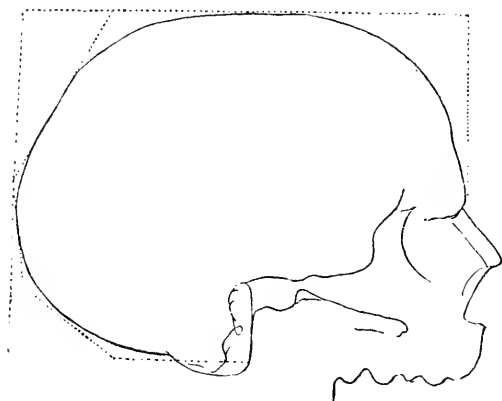


FIG. 27.—ACMONOIDES (TVER).

occipital is raised on an inclined plane, very sloping, while the base of the cranium does not rest upon the same plane through its entire length.



FIG. 28.—ACMONOIDES SICULUS.

12th. ACMONOID (*acmonoides*) (Figs. 27, 28).

It is not difficult to distinguish this variety with its anvil-like form. Once seen, it becomes impressed on the memory by the singularity



of its shape. A long cranium, the norma verticalis not elliptical nor ovoid, because the sides are straight, a slight swelling of the parietal protuberances situated very far back, and the occipital resembling a quadrangular pyramid, leaning slightly on its cranial base. The cranium is high on the side, the forehead vertically inclined, but a little elevated; the arch is on the horizontal plane, abruptly inclined at the summit of the occipital pyramid, the extremity or protuberance of the occipital level. It has quite a large capacity. The types given here are derived (Fig. 27) from the Russian Kourgans, (Fig. 28) from modern Sicily.

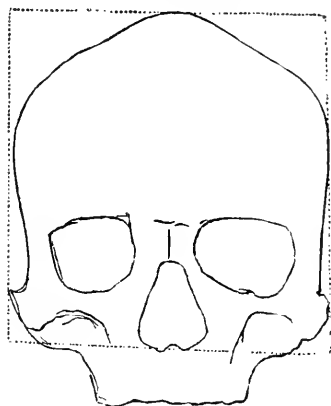


FIG. 29.—LOPHOCEPHALUS.

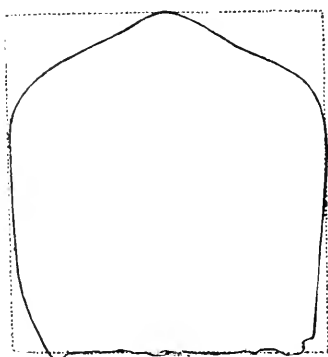


FIG. 30.—LOPHOCEPHALUS.

### 13th. LOPHOCEPHALIC (*lophocephalus*) (Figs. 29, 30).

This variety has a conspicuous trait not seen from the norma verticalis nor norma lateralis, but from the norma facialis and the norma occipitalis. This is, as shown in Figs. 29 and 30, the median eminence extending from the forehead to the sagittal. This eminence, which I call *lophus* (*lophos*), and which is described by other anthropologists as “crania with the arch of the backbone of an ass,” or “arch like the keel of a ship,” commences in the upper part of the frontal, at the place where the frontal curve first becomes horizontal. It is an elevation of the median portion, with lateral depressions amounting to a slight concavity, which reaches the coronal, the highest part of the eminence and surpasses it, invading the sagittal, where it terminates at the apex of the triangle, gradually disappearing.

This variety I have described among the crania of Melanesia, and the type which I give is from there; but it is not limited to that region and presents certain variations.

14th. CHOMATOCEPHALUS (*chomatocephalus*) (Fig. 31).

We call "tumulus-like" (*chomo*) that cranium which is elevated like a hill upon a horizontal plane passing through the orbital arches. It is not spherical, and slopes almost equally on all sides, starting at the summit of the cranial arch, which is much elevated, as seen in Fig. 31. Such a cranial arch may not always be regular in its inclinations, nor perfectly symmetrical, and not like a hill or gradual elevations of land, but should resemble a high elevation, and be almost disproportionate to the face. The type presented is from Melanesia. It is large, with a large capacity; there are also smaller and different types, both in the same region and elsewhere.

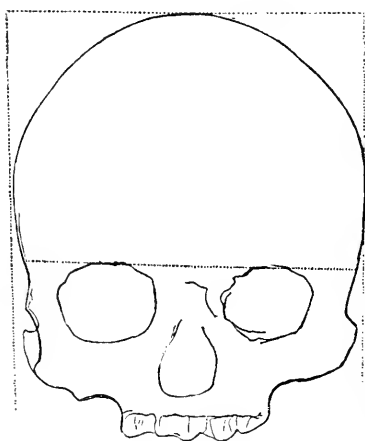


FIG. 31.—CHOMATOCEPHALUS.

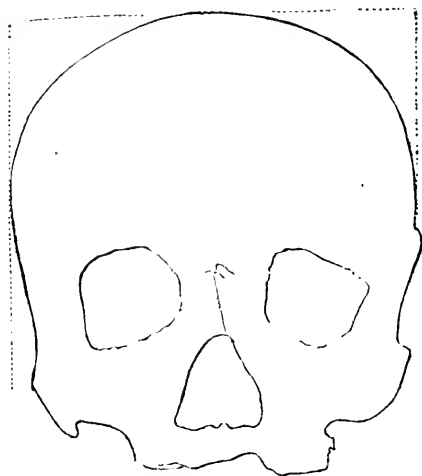


FIG. 32.—PLATYCEPHALUS.

15th. PLATYCEPHALIC (*platycephalus*).

Platycephaly usually concerns the arch of the cranium only. It is flat, in a relative degree to the usual convexity. In fact it is a curve of the cranial arch which resembles an arc of a circle with a large radius; the platycephalic forms will be distinguishable in

proportion as this idea is considered. As a rule the cranium is also wide in its transverse diameter, and hence it is also relatively short, as seen in the brachycephalic, Figs. 32, 33 and 34. Fig. 32, which is the profile of an Italian cranium, resembles strongly Fig. 33, which is a Russo-Kourgan; Fig. 34 is the norma verticalis of the latter and shows its relative width.

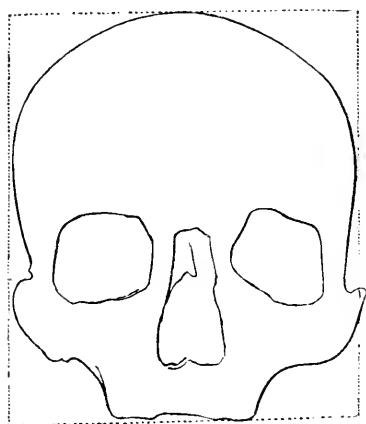


FIG. 33.—PLATYCEPH. BOGDANOVII.

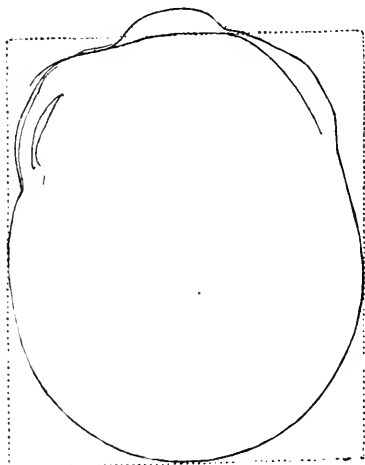


FIG. 34.—PLATYCEPH. BOGDANOVII.

This characteristic is so evident and so much a part of the cranial form, to which a pathological signification has been erroneously attributed, that it alone is sufficient to constitute a distinct variety. It is easy to distinguish a cranium by such a characteristic without directly considering the norma facialis or norma occipitalis, and hence it is a good characteristic for classification. Among platycephalous forms there is one which is prominent on account of the unusual lowness of the arch, besides being very flat. It presents a small forehead and a general depression of the cranium from the orbital apophysis to the superior plane. The top of the cranium resembles a flat cake or a bun, whence the name *placuntoides* which I have given to it, that is, the form of a flat cake (Fig. 35). There are also platycephali with narrow foreheads, which I will consider later.

16th. SKOPELOID (*skopeloides*) (Fig. 36).

The form which I call "rock-like" (*skopelos*) is very curious. It has a summit on the posterior part of the cranium which slopes from every side, and at the occiput descends rapidly to the base. The cranium is large, wide at the base, with a narrow forehead, and the frontal slightly sloping, following the inclined plane of the posterior summit.

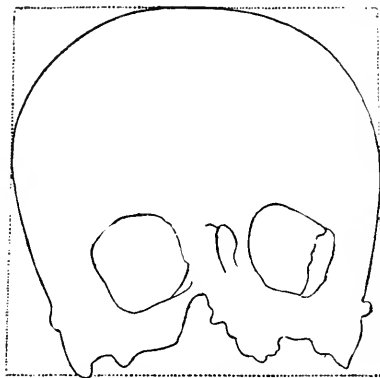


FIG. 35.—PLACUNTOIDES.

This form is difficult to describe, and Fig. 36 gives an imperfect idea of it.

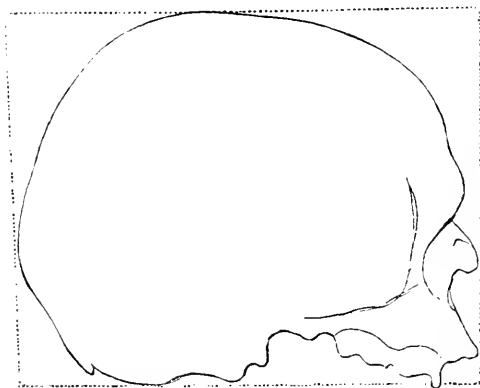


FIG. 36.—SKOPELOIDES SAMNITICUS.

Of this variety, so characteristic and quite common in Samos, I have seen some which are microcephalous, in Samos and likewise in the Russian Kourgans, although there very rare.

The sixteen human varieties above described I have determined, after observations of more than 3500 crania, principally from the Mediterranean, prehistoric tombs, and modern Russia, the crania of the Kourgans, and from some ancient cemeteries in Moscow and the Chersonesus, and from Melanesia. I can affirm nothing of the entire number of human varieties, nor of their distribution, before making new and direct personal observations in the rest of Europe and in other parts of the world; I wait in confidence and with the earnest desire of making such observations. I affirm with some personal satisfaction that, as regards the new anthropological method, I have surmounted its uncertainties. The number of varieties has been much reduced, and they are separated by definite and recognizable characteristics.

I cannot affirm that new varieties may not be found even in the Mediterranean field, where I have chiefly extended my researches. If they should be found they would be few, and probably brought from other localities.

## II.

### *Subvarieties.*

Though the number of varieties which I have until now determined in the Mediterranean and Russia, together with some from Melanesia, is limited to sixteen only, the subvarieties are much more numerous. Subvarieties should first of all preserve the characteristics of the variety of which they are a variation, and should have some other characteristic, which must not be transitory and individual, but fixed and hereditary. Groups of subvarieties must constitute real groups; the variety is the principal denomination of characteristics common to many subvarieties, which add to the primary or dominant characteristic one or several new characteristics which separate the subvarieties from each other, as the following scheme exhibits:

Variety: A.

Subvariety:  $A + a$ ,  $A + b$ ,  $A + c$ ,  $A + d$ , and so on.

While the characteristic A gives the name to the variety, the less general characteristics a, b, c, d give the subvarieties of A.

The same relation is found in the animal kingdom between genera and species, or between species and varieties; in the first place, the universal characteristics of the genus are limited by those of the species; in the second, those of the species are restricted by those of the varieties, and those of the variety by the subvarieties. I have above stated that while in my opinion the name of variety is general in its meaning, and therefore also provisional, it may remain definitive by further study and assume a fixed signification. Different results may be reached, but the classification will remain unaltered, because the characteristics will continue stable and the method unchanged.

In determining the characteristics of numerous series of crania, and in arranging groups of one variety, another plan occurred to me, that of finding characteristics which separate a subvariety into groups of a third order, meaning by a group of the 1st order the variety; then we shall have a plan like the following:

1st. Variety: A.

2d. Subvariety:  $A + a$ ,  $A + b$ ,  $A + c$ , etc.

3d. Sub-subvariety:  $A + a + \alpha$ ,  $A + a + \beta$ ,  $A + a + \gamma$ .

The characteristics  $\alpha$ ,  $\beta$ ,  $\gamma$  are not transitory; they are stable, and, on this account, of the same type as those which distinguish the subvarieties  $a$ ,  $b$ ,  $c$ , etc.

It is easy to answer an inquiry as to the manner of distinguishing these characteristics: individual variations are not repeated, and they therefore do not occur in many individuals, unless accidentally; not only do they cause little divergence from the typical forms, they constitute oscillations of the same form recognizable as such. It is not so with the characteristics of subgroups of the 2d or 3d order; they alter the fundamental form in some part, and are repeated in groups composed of several individual elements.

We have seen how we may determine varieties, which in a great measure assume geometrical forms and receive corresponding names, because of their approximation to bodies with well-known geometrical characters. We have also seen that we can determine the form of this irregular body, the brain, either by the vertical or lateral norm, or in some cases by the anterior or posterior aspect. Besides the normae which determine the variety, there remain other normae which have various characters, and can therefore complete the craniological type or show its variations beyond the

primary character which places it in a given variety. An ellipsoid, regarded vertically, may have different *normae laterales*, at the same time remaining an ellipsoid; it may also have other characteristics, visible from the *norma occipitalis*, which make it vary from another cranium, also ellipsoid, with a different *norma occipitalis*. There may also be variation in the same *norma* which gives the fundamental form; for example, the ellipsoid (Fig. 38) is shorter and relatively wider than the one beside it (Fig. 37),

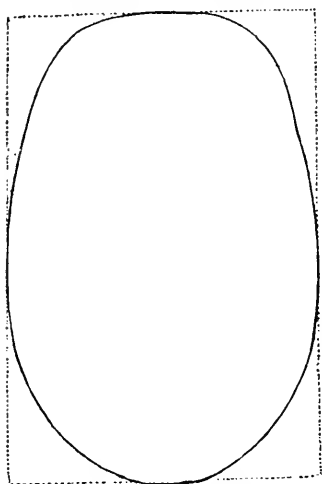


FIG. 37.—DOLICHELLIPSOIDES.

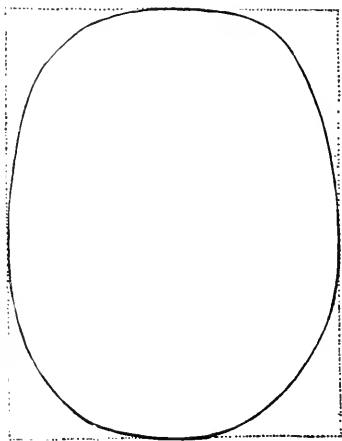


FIG. 38.—BRACHYELLIPSOIDES.

which is therefore a “dolichellipsoid,” while those wide and short, like Fig. 38, we may call “brachyellipsoids.” Such variations of elliptical forms correspond to the structure of the cranium, and therefore constitute subvarieties.

Following the order above carried out in the varieties, I commence with the ellipsoid.

## I. ELLIPSOIDES.

### 1st. *Ellips. depressus*.

This is visible from the *norma lateralis* and also from the *norma anterior* (Fig. 39). Cranium low from the vertex to the occipital base, as if crushed in every direction from the frontal and lateral sides, and therefore with a narrow, retreating forehead, of curved

form; the same of the occiput. This curious and characteristic form is subject to variations which would take too long to describe here.

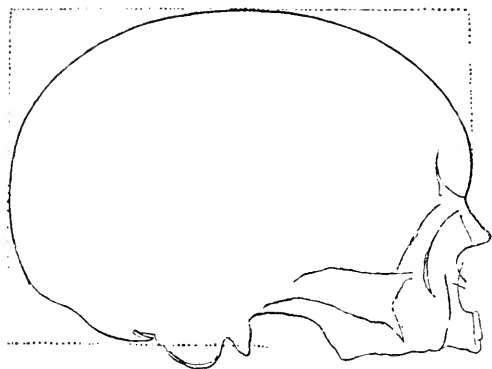


FIG. 39.—ELLIPS. DEPRESSUS.

2d. *Ellips. isopericampylus* (Fig. 40).

*Isopericampylus* signifies "with equal curves all around"; the character of this subvariety is especially that the form is handsome and perfect. It may have variations in the form of the ellipse and in some other characters.

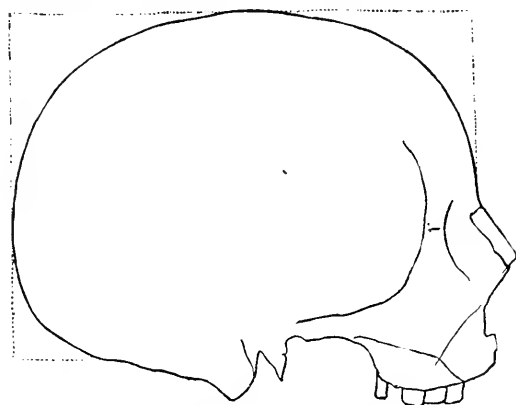


FIG. 40.—ELLIPS. ISOPERICAMPYLUS.

3d. *Ellips. embolicus*.

From *embolus*, prow, because the occipital decline, which commences well forward, reaches as far as the cranial base, and such



a projection has the apparent form of a ship's prow. I at first called this form *emboloides meridionalis*, because I had observed it among the crania of Southern Italy. I found it again in Russia

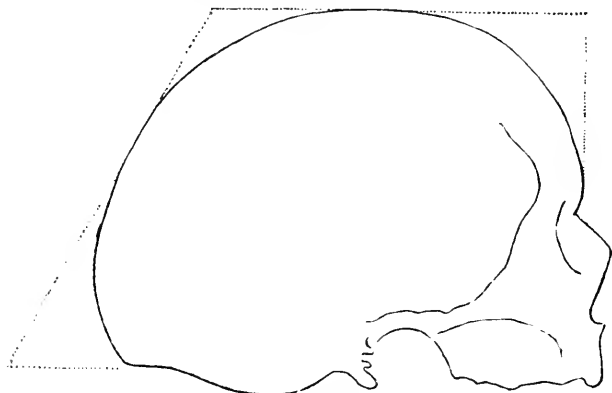


FIG. 41.—ELLIPS. EMBOLICUS.

among the Kourgan crania, among Etruscan crania, ancient Roman, and finally at Novilara (Pesaro) in tombs perhaps of the

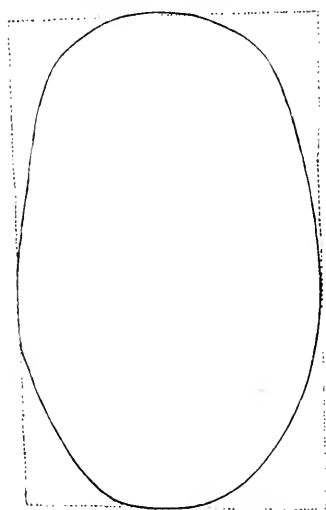


FIG. 42.—STENELLIPS. EMBOLICUS.

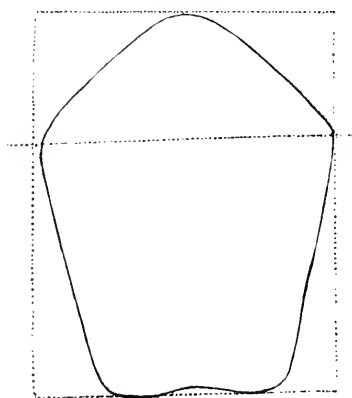


FIG. 43.—STENELLIPS. HYPSTEGOIDES.

5th century before the Christian era. Fig. 41 is the profile of a cranium of the Kourgans of Tver. This cranium, that is, this

cranial form with definite ellipses, is long and at times exceeds 200 mm., and differs in width. In the meridional emboloid it is 135-138 mm., but in others is below 130 mm.; hence the name of *stenellipsoides embolicus* which I have given it, as in the cranium from Novilara which I have shown here (Fig. 42).

4th. *Ellips. hypsistegoides* (Fig. 43).

This form is visible from the posterior norma of the cranium, as in Fig. 43 (cranium from Novilara). The arch is constructed like a roof in the example here given, and the height of the cranium from the base to the vertex is considerable. There are *stegoid* varieties also, that is, with a roof-like arch, not very high.

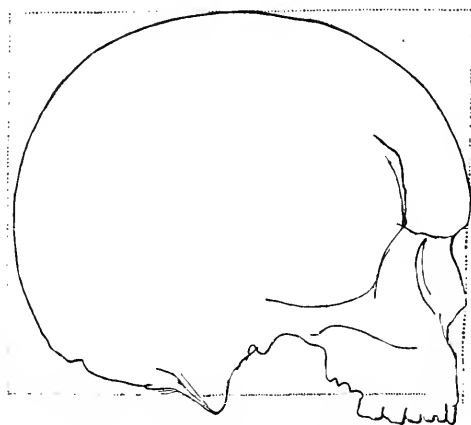


FIG. 44.—ELLIPS. CORYTHOCEPHALUS.

5th. *Ellips. corythocephalus* (Fig. 44).

"Helmet-like cranium," high, with a fine curve from the forehead to the occiput as far as the base, of large capacity, and flat at the sides. This gives it the appearance of a helmet. I found it first among ancient Egyptian crania, whence its name of *aegyptiacus*; then among the Kourgan crania.

6th. *Ellips. epiopisthius*. That is, a cranium of elliptical form in which the level rises from the frontal towards the posterior part, so that the latter appears to be raised (Fig. 45).

7th. *Ellips. scalenus*. The *epiopisthius* can also be, as in this case, *scalenus*, a rapid obliquity from the occipital slope. But the *cranio-scalenus* can also be found without being *epiopisthius*, and

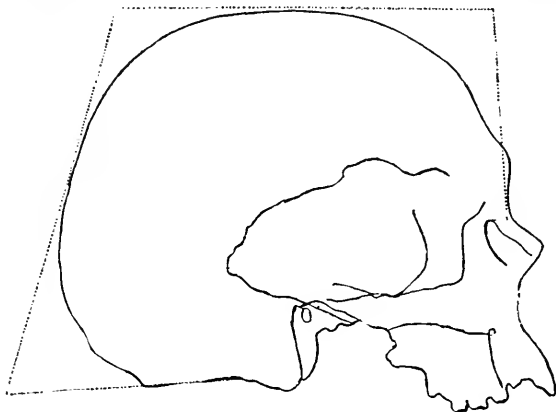


FIG. 45.—ELLIPS. EPIOPISTHIUS.

*vice versa*. These two characteristics appear separately and together in other varieties, as in the ovoid, the platycephalus, and in the ellipsoidal subvariety. This may also be said of the roof-like form, or *stegoid*, and of the *hypsistegoid*.

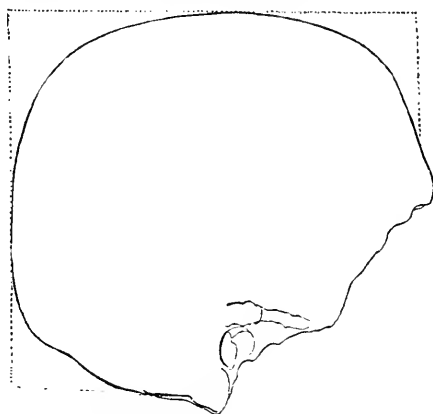


FIG. 46.—ELLIPS. TETRAGONALIS.

8th. *Ellips. tetragonalis* (Fig. 46).

This ellipsoidal form is very characteristic in its *norma lateralis*,

which has the appearance of a tetragon, whence its name. The cranium is high, the forehead as a rule erect, the occiput perpendicular and very convex and depressed at the sides. It may be confused with the cuboid when seen only from the norma lateralis. But I must now omit a series of subgroups and limit myself to the principal forms.

II. *Pentagonoides*.—With regard to varieties, I have distinguished various pentagonoids, *acutus*, *obtusus*, *oblongus*, *brachypentagonoides*; and there may be *stegoids*, *cristati*, etc.

III. *Rhomboides*.—The rhomboids are also short, *brachyrhomboides*, or elongated in the anterior part, *oblongus*.

IV. *Ovoides*.—Subvarieties of ovoids are found with wedge-like occiput, *cuneatus*, *scalenus*, *stegoides*, *depressus*.

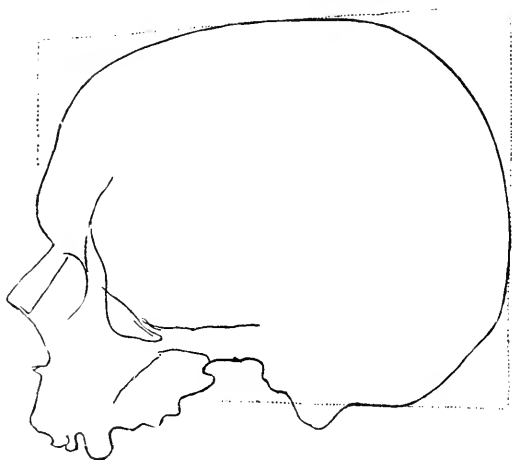


FIG. 47.—SPHEN. TETRAGONUS.

V. *Sphenoides*.—By the norma verticalis I have distinguished *sphenoides*, *stenometopus*, *sph. rotundus*, *sph. spelatus*, *sph. megas*, *sph. oblongus*; an important subvariety is found in *tetragonus* (Fig. 47), which is not only sphenoidal in the vertical, but also in the lateral, and has prominent corners, rendering the vertex and sides plane.

There is likewise a sphenoid, *cyrtcephalus*, which has a convexity extending from the frontal and parietals to the vertex,

resembling a protuberance, though not so pronounced as to constitute a *crista* or a *lophos*; if these two characteristics are found, the *sph.* is *cristatus* or *lophoides* (Fig. 48).

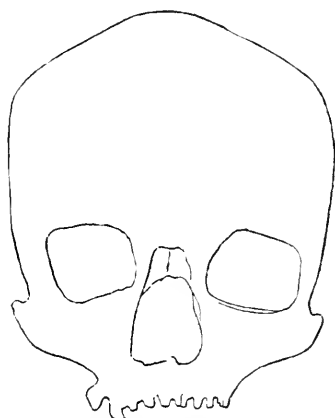


FIG. 48.—SPHEN. CRISTATUS.

VI. *Sphaeroides*.—I have given the principal variations of this variety, that is:

- a) *sphaerotocephalus*;
- b) *sphaeroides, hemisphaeroides*;
- c) *strongylocephalus* (see above).

VII. *Byrsoides*.—So far I have only found one variation from the *siculus*, that is, the *aegyptiacus*, which is a little narrower (see above).

VIII., IX., X. *Parallelepipedoides, Cylindroides, Cuboides* (see varieties).

XI. *Trapezoides*.—I have already distinguished two subvarieties with the names of *Trap. sardinensis* and *Trap. africanus*. These are the most typical and commonest variations; in my catalogue of Russian varieties several other secondary forms are found, of which the commonest is *trap. rotundatus*.

There is a subvariety which I considered during my first observations as a distinct variety, and which I had named *Pyrgoides*,

a cranium resembling the form of a tower. This cranium is also a trapezoid, but it is larger, the occiput is high and perpendicular, so that the vertex of the cranium coincides very far back with the bregma. It is large enough to appear spheroid, the anteposterior declivity slopes uniformly from the back.

I preserve the name *Pyrgoides* for such forms because the occipital looks like the wall of a tower, high and quadrangular; but I consider it a subvariety of the trapezoid. I have noticed variations in *Pyrg. romanus*. The type in Fig. 49 is a *cyrtocephalus*, so called on account of the fronto-bregmatic protuberance, a *rotundatus* on account of the truncated corners and the convex faces.

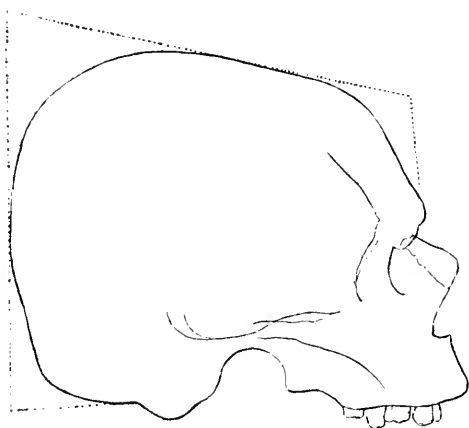


FIG. 49.—PYRGOIDES.

XII. *Acmonoides*.—Of this singular variety I have found sub-varieties: a) *siculus*, which is the typical form described; b) *megalomotopus*, or having a large, wide forehead; c) *obtusius*, on account of the rounded corners; d) *stegoides*, on account of the roof-like arch; e) *subtilis*, because narrower than the type; f) *proophyrocus*, because it has prominent frontal sinuses which do not exist in the type.

XIII. *Lophicephalus*.—This variety offers some variations from the type from Melanesia before presented; its principal characteristic does not consist in the *lophos*, but in the cranial

form being a little larger. It is found among the Kourgans (Fig. 50); the width is greater posteriorly, and the lateral parts more convex, *loph. kurganicus*.

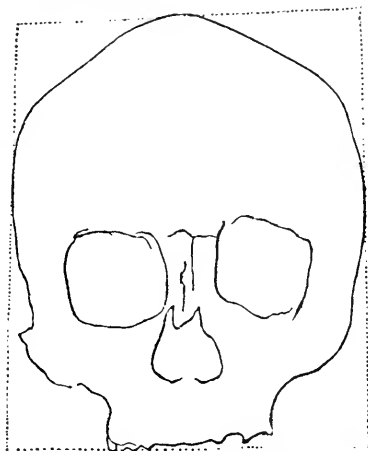


FIG. 50.—LOPHOC. KURGANICUS.

#### XIV. *Chomatocephalus*.

I have found subgroups with the following characteristics :

a) *Chom. angulosus*, because it has a surface with angular projections.

b) *Chom. summus*, on account of its great height.

c) *Chom. cristatus*, on account of its crest-like summit.

d) *Chom. sphenoidalis*, for its wedge-like form as observed from the norma verticalis.

XV. *Platycephalus*.—The varieties with most subvarieties are the *Ellipsoides*, the *Sphenoides*, and the *Platycephalus*. Of the *Platyc.* I have so far been able to distinguish 22 varieties, of which several also have subgroups, as the *Isobathyplatycephalus*, which I have called *siculus* because first found in the tombs of the neolithic age in Sicily (Fig. 51). We find:

a) *Platyc. cuneatus*; b) *platyc. humilus*; c) *stenometopus*; d) *platyc. brachymetopus*; e) *curyplatymetopus*; f) *platyc. embolicus*; g) *platyc. rotundus*; h) *platyc. scalenus*, and so on.

XVI. *Scopeloides*.—A common form in *Samos*, and should be more sought after in Italy.

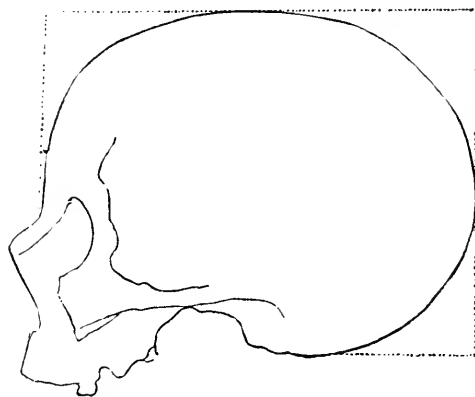


FIG. 51.—ISOBATHYPLATYC. SICULUS.

In ending this description of subvarieties, at present limited to those of the sixteen human varieties (and which I consider incomplete in number, just as I have considered incomplete the number of varieties of the Mediterranean and Kourgans of Russia, where I have found the varieties described), I should add, in order to complete the picture of subvarieties, another characteristic of classification, of which I have above spoken, the volume of the cranium.

As I have said, what is well known in regard to other animals occurs in man, that large and small varieties are found, both in stature and in the volume of the cranium, and these differences in size and volume are not indications of functional superiority or of priority. The functions of the brain of 1200 gr. can be just as perfect as those of a brain of 1600 gr., and it is known that not all large and voluminous brains are those of great men, nor are those of inferior or commonplace human types small. I have found ellipsoids, cuboids, ovoids, pentagonoids, platycephali, trapezoids, large, medium, and small, with complete and perfect structures in the large as well as in the small and microcephalic varieties; for this reason I have thought it wise to consider types of different volume or cranial capacity as subvarieties, and not to confuse the capacity of one with another.



I have also found that certain cranial types have a special capacity which does not belong to another type. Thus the trapezoids have a small capacity, between elatto- and microcephalic, and never exceed that limit; that of the pyrgoids is greater; the stenocephali have a small capacity; the coritocephali are megalcephalic, and so on.

I have adopted the words *megas*, *magnus*, *maximus* for the large and largest varieties, *medius* for the medium, and *parvus* and *micros* for the small and smallest varieties. In respect to the capacity when measured, we may practically consider *micros* as far as the average of 1150 cc.; *parvus*, as far as the average 1350 cc.; *megas*, from 1500 up; *maximus*, beyond 1700 cc. Thus the number of subvarieties becomes increased.

### III.

#### *Nomenclature.*

Nomenclature is necessary in the classification of animals, of plants and minerals. Names aid to discern forms, to recognize general characteristics by means of which series and groups are formed, to distinguish series from each other. Without names we should not know of what we speak. Thus in the classification of human varieties and subvarieties it is necessary to adopt technical names in order to indicate them; although we may but imperfectly express the entire conception of the form which we wish to indicate.

For this purpose I have selected words from the Greek and secondarily from the Latin languages, because Greek words are better adapted for proper names, and are easily constructed, while words in use in a modern language would be difficult to foreigners, and having a vulgar signification, would be equivocal; finally, because many languages derive names of geometrical forms from Greek and Latin, and hence such can easily be understood.

It may appear that I have too much increased the number of technical names in my earlier memoir, *Human Varieties of Melanesia*. In a measure that is true, but most of the words for each variety were in use previously. *Brachy*, *meso*, *dolichocephalo*, *hypsi*, *chamecephalo*, *lepto*, *chameprosopo*, *lepto*, *meso*, *platyrinno*,

*brachy*, *leptostafilino* and the like are not my words. It appeared that the vocabulary would be enormous and sibylline when other expressions were added to the name of *stenocephalo*, etc. The French school, as regards nomenclature, is the most exaggerated. I need but state that besides the words above given and common to all anthropological schools, it has *basion*, *episthion*, *pterion*, *obelion*, *inion*, *nasion*, *ophryon*, *metopion*, *stphanion* and the like. If in adopting the zoological method which I have indicated we abandon craniometry, and with it its nomenclature, there will remain but few technical terms for the indications of varieties and subvarieties, and then nomenclature will be brief and significative. Whoever reads my Memoirs from the first, that upon the Melan-esians, to the last, upon "microcephalic varieties," will observe how I have little by little eliminated names and confusing and wearisome measurements, and have reduced classification by technical terms for nomenclature to the greatest simplicity.

Objections made against the nomenclature which I have introduced can also be applied to that used in zoology and botany and in all the sciences which have one. An important objection seems to me that of Professor Benedict of Vienna, who would like to abolish every word of Greek and Latin origin, because they are dead languages which in a few years will no longer be taught in schools of science. I agree with him. But, as I have above said, it matters little whether a technical name of a variety be understood in its signification provided that the variety denominated be known by means of the name, and nothing more, when it refers to a determinate form. Moreover, a reform in classification should not suffer through a difficulty in names, which, if they were Italian, would not be easily accepted and understood by strangers. Greek and Latin have at least the advantage of being languages which can now be universally retained for the sciences. The objections, or rather I should say the observations, made by Hovelacque and Mantegazza are of no value and do not merit attention.

I at first adopted technical names Italianized, but afterwards, in order to render the meaning easy to foreigners, I adopted the Latinized form, which has the advantage of preserving the original vowels and consonants. The naturalist, accustomed to zoological nomenclature, finds nothing new, much less strange, in this

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method, and the anthropologist is a naturalist who is occupied exclusively with man.

I consider it useful and opportune to prepare catalogues of the varieties and subvarieties, and to record the geographical distribution of forms; they are pictures which render two facts evident, the number of ethnic elements and their dispersion.

I hope by this method and by these principles a systematic anthropology may be constituted, which may be the foundation for scientific researches upon the origin of human races, upon their number and distribution, upon their crossings, and, finally, upon the possible solution of the problems of the unity or plurality of the species.



SMITHSONIAN MISCELLANEOUS COLLECTIONS

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# BIBLIOGRAPHY

OF

# ACETO ACETIC ESTER

AND ITS DERIVATIVES

BY

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1894

## LETTER OF TRANSMITTAL.

NEW YORK, August 22, 1892.

The Committee of the American Association for the Advancement of Science having charge of Indexing Chemical Literature has voted to recommend to the Smithsonian Institution for publication the following Index :—

Bibliography of Aceto Acetic Ester and its Derivatives, by P. H. Seymour, M. S., Assistant in General Chemistry, University of Michigan.

This work was compiled under the direction of Prof. Albert B. Prescott, Ph. D., a member of this Committee.

H. CARRINGTON BOLTON,  
*Chairman.*

TO THE SECRETARY OF THE  
SMITHSONIAN INSTITUTION.





## PREFACE.

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It is the purpose of this brief contribution to point out the existing literature upon acetoacetic ester, rather than to make an addition to this literature. The outlines of memoirs are given, not to enable the reader to do without the originals, but to help him to find just the ones he may require. To this end it has been undertaken to furnish a description, without the detail of a condensation, of so much literary material as has been cited. The subject is one so far interwoven with research upon organic oxygen derivatives in general that its boundaries have been often drawn at a venture. In questions upon the subject-matter Mr. Seymour has had the benefit of consultation with Professor Paul C. Freer, of this University, who has carried on investigations of acetoacetic ester for some years. For the plan of the bibliography, whatever defects the plan may have, the undersigned acknowledges himself responsible. In the execution of the task Mr. Seymour has devoted studious care, with clear critical inquiry on his own part, from first to last. And his work is offered with confidence by the undersigned, to the Committee on Indexing Chemical Literature, for issue under the beneficent provisions of THE SMITHSONIAN INSTITUTION, to whose time-saving publications chemists are so greatly indebted.

ALBERT B. PRESCOTT.

UNIVERSITY OF MICHIGAN,  
August, 1892.



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## INTRODUCTION.

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In the following work the articles were abstracted with reference to the subject of the bibliography, consequently some articles were abstracted only in part; that is, omitting what had no relation to acetoacetic ester. The word "ester" has been used to mean an acid in which the carboxylic hydrogen has been replaced by an alkyl radical, and where the alkyl radical is not specified, ethyl is understood.

The bibliography is arranged in chronological order, with author and subject indices appended.

All references given were verified, except where otherwise stated.

The reference given first in each case is the original publication, the others are reprints or abstracts.

The literature on the subject begins in 1840.

I wish to express my gratitude to Professors Prescott and Freer for direction and aid in the work.

PAUL H. SEYMOUR.

UNIVERSITY OF MICHIGAN,  
June 11, 1892.

## LIST OF PERIODICALS CONSULTED.

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The following periodicals were examined carefully for articles upon the subject of the bibliography from the first volume in each case to the end of 1891 :

- Annalen der Chemie und Pharmacie* (Vol. I., 1832).  
*Berichte der deutschen Chemischen Gesellschaft* (Vol. I., 1868).  
\**Jahresbericht über die Fortschritte der Chemie* (Vol. I., 1847).  
*Journal of the Chemical Society* (Vol. I., 1849).  
*Bulletin de la Société chimique de Paris* (Vol. I., 1864).

The following were consulted upon references :

- Comptes rendus de l'Académie des Sciences.*  
*Annalen der Physik und Chemie*, **Poggendorff**.  
*Journal of the American Chemical Society.*  
*Journal für praktische Chemie.*  
*Archiv der Pharmacie.*  
*Jahresbericht über die Fortschritte der Chemie*, **Berzelius**.  
*Chemical News.*  
*American Chemical Journal.*  
*Annales de Chimie et de Physique.*

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\* Of this 1887 was the last volume published.

# BIBLIOGRAPHY

## OF

# ACETO ACETIC ESTER.

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**LÖWIG, CARL AND SAL. WEIDEMANN, 1840.**

Ann. der Phys. Pogg. **50**, 95-125 ; Ann. Chem. **36**, 297-304 ; Berzelius' Jsb. **21**, 425.

### Action of Potassium and Sodium on Some Ethers.

Potassium attacks acetic ester at once and is dissolved. No gas is given off ; the mass solidifies and is found to be composed of potassium ethoxid and a compound of acetyl and oxygen, having less oxygen than acetic ester ; in other words the potassium abstracts oxygen from acetic ester. The product obtained, treated with sulfuric acid, gives acetic acid. The author decides that it is probably "Hypoacetous acid" (unteracetylig-saure)  $C_4 H_6 O_{1\frac{1}{2}}$ .

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**GEUTHER, A., 1863.**

Arch. der Pharm. **116**, 97-110 ; Jsb. Chem. 1863, 323.

### Researches Upon Monobasic Acids.

Acetic ester was boiled with sodium and a stream of hydrogen passed through. Sodium acetate and a compound  $*C_{12} H_9 Na O_6$  were formed. This compound was named dimethylen-carbonethylen ether sodium, as

the author supposed it to be formed thus:— $2 *C_2 H_2, C_2 O_2 \left. \begin{array}{l} \text{) OH} \\ \text{) OH, } C_4 \end{array} \right\} Na O$

$H_4 + 2 Na = C_2 H_2, C_2 O_2 \left. \begin{array}{l} \text{) Na O} \\ \text{) H O, } C_4 H_4 + C_4 H_5 Na O_2 + H_2. \end{array} \right\}$  By treating this compound with ethyl iodid he formed dimethylen-carbonethylen ether  $*C_{16} H_{14} O_6$ , boiling at  $198^\circ$  with a specific gravity of .998 at  $12^\circ$ . By using methyl iodid dimethylen-carbonmethylen ether  $*C_{14} H_{12} O_6$  boiling at  $186.8^\circ$  was produced. By the action of ammonia on the former, two bodies were formed ;— $*C_{16} H_{15} NO_4$ , insoluble in water, melting at  $59.5^\circ$ , and  $C_{12} H_{11} *NO_4$ , soluble in water, melting at  $90^\circ$  and subliming at  $100^\circ$ . By passing carbon dioxid through  $*C_{12} H_9 Na O_6, C_{12} H_{10} O_6$  was produced. It colors ferric chlorid, a dark violet.

$*C = 6 ; O = 8.$

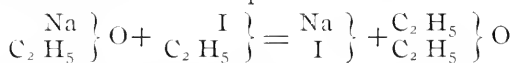
**WANKLYN, A., 1864.**

J. Chem. Soc. **17**, 371-377 ; Chem. News. **10**, 195 ; Jsb. Chem. 1864, 461.

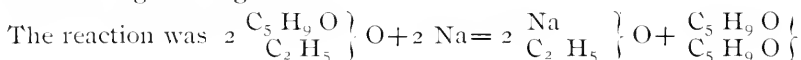
**Some Actions of Sodium and Sodethoxid.**

The difference is shown between treating sodethoxid with an alkyl iodid and an alkyl acetate.

In the first case sodium iodid is produced thus :



In the second case the sodium replaces the acetyl group and not the ethyl. This could not be shown in acetic ester, therefore valeric ester was worked with. It was treated with metallic sodium, reaction took place and no gas was given off.

**GEUTHER, A., 1866.**

Arch. der Pharm. **125**, 29-50, and **201**, 223 ; J. Prakt. Chem. **99** 113-125 ; Jsb. Chem. 1865, 302 ; Bull. Soc. chim. **6**, 222.

**Acetic Acid.**

Acetic ester was treated with sodium and  $\text{C}_6\text{H}_9\text{NaO}_3$  was produced. By boiling with water it was decomposed into acetone, alcohol, carbon dioxid and sodium carbonate.  $\text{C}_6\text{H}_{10}\text{O}_3$  was produced from its sodium compound by treating with hydrochloric acid, carbon dioxid or acetic acid, when it was called by the author ethyl-diacetic acid ; it has a specific gravity of 1.03 at  $5^\circ$ , boils at  $180.8^\circ$  and reddens litmus only when water is added. In obtaining it some dehydracetic acid was always formed. It has the composition  $\text{C}_8\text{H}_8\text{O}_4$  and melts at  $108.5^\circ$  and boils at  $269.6^\circ$ . The barium and copper compounds of ethyl-diacetic acid and the barium, sodium and calcium salts of dehydracetic acid were described. Ethyl-diacetic ethyl  $\text{C}_8\text{H}_{14}\text{O}_3$  produced by ethyl iodid boils at  $198^\circ$  and colors ferricchlorid blue. Ethyl-diacetic methyl  $\text{C}_7\text{H}_{12}\text{O}_3$  boils at  $186.8^\circ$  has a specific gravity of 1.009 at  $6^\circ$  and colors ferric chlorid a deep blue.

**FRANKLAND, E., AND B. F. DUPPA, 1866.**

J. Chem. Soc. **19**, 395-434 ; Ann. Chem. **138**, 204-225 and 328-360 ; Phil. Trans. Lond. **156**, 37 ; Jsb. Chem. 1865, 304.

**Synthetical Researches on Esters. Part I.**

Acetic ester was made from sodium acetate, alcohol and sulfuric acid. It was treated with sodium when an action took place and hydrogen was given off. The product was treated with ethyl iodid and the



result was a small amount of  $C_6H_9(C_2H_5)O_3$  and a larger amount of  $C_6H_8(C_2H_5)_2O_3$ . The latter is colorless, insoluble in water, miscible with alcohol and ether, boils at  $137.5^\circ$ – $139^\circ$  and has a specific gravity of .8171 at  $22^\circ$ .

Ethylic ethacetone carbonate  $C_6H_9(C_2H_5)O_3$  is colorless, almost insoluble in water, miscible with alcohol and ether, boils at  $195^\circ$  and distils unchanged, it has a specific gravity of .9834 at  $16^\circ$ . When saponified with a water solution of potassium hydroxid, ethyl acetone,  $CH_3COCH_2(C_2H_5)$ , is produced which boils at  $101^\circ$  and has a specific gravity of .8046 at  $22^\circ$ . Both of these acetones have the smell and the taste of camphor. The di-methyl derivative of acetoacetic ester (as it is now known) was prepared, the reactions given were  $2CH_3CO_2C_2H_5 + 2Na = CH_3COCH_2Na + CH_3CO_2C_2H_5 + C_2H_5OH + H_2$  and  $CH_3COCH_2Na + CH_3CO_2C_2H_5 + 2CH_3I = CH_3COCH_2CH_3 + 2NaI$ . Some of the mono methyl derivative was also formed but was decomposed by a water solution of potassium hydroxid. Methyl acetone,  $CH_3COCH_2CH_3$ , boils at  $81^\circ$  and has a specific gravity of .8125 at  $13^\circ$ . Dimethyl acetone,  $CH_3COCH_2CH_2CH_3$ , boils at  $93^\circ$  and has a specific gravity of .8099 at  $13^\circ$ .

Ethylic dimethyl acetone carbonate,  $CH_3COCH_2CH_2CO_2C_2H_5$ , boils at  $184^\circ$  and has a specific gravity of .9913 at  $16^\circ$ .

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### BRANDES, R., 1866.

Arch. der Pharm. [2] **129**, 193-212; Jsb. Chem. 1866, 305; Bull. Soc. chim. **7**, 501.

### Acetic Acid.

Methylen-dimethylen carboxylic acid,  $C_5H_8O_3$  (acetoacetic methyl ester), is produced from acetic methyl ester and sodium, sodmethoxid and hydrogen being formed in the reaction. It is supposed to be an acid, and to be acetic acid in which two hydrogen atoms of the methyl group are replaced, one by methyl and the other by acetyl. It is colorless, boils at  $169^\circ$ – $170^\circ$ , and has a specific gravity of 1.037 at  $9^\circ$ . Blue litmus is scarcely changed by it until water is added. Alkalis and acids decompose it into acetone, carbon dioxid and methyl alcohol. The copper salt was made and described. Methylen-dimethylen carboxylic acid ethylen (ethyl-acetoacetic methyl ester), prepared from the former by treating with sodium and then with ethyl iodid, is colorless, boils at  $189.7^\circ$  and has a specific gravity of .995 at  $14^\circ$ . It is isomeric with Geuther's ethyl-dimethylen carboxylic acid methylen (methyl acetoacetic ester). By using methyl iodid methylen-dimethylen carboxylic acid methylen (methyl acetoacetic methyl ester), was produced, it boils

at  $177.4^{\circ}$  and has a specific gravity of 1.020 at  $9^{\circ}$ . Methylene-dimethylen carboxylic acid ethylen treated with ammonia gives two compounds;  $C_7H_{13}NO_2$ , which is insoluble in water, and  $C_5H_9NO_2$ , which is soluble in water. When the above esters are distilled some dehydracetic acid  $C_8H_8O_4$  is formed as a solid in the flask.

Geuther appends a note to this article in which he gives his opinion as to the constitution of dehydracetic acid. He supposes it to be acetic acid in which two hydrogen atoms have been replaced by acryl,  $C_3H_3O$ , thus:  $CH(C_3H_3O)_2CO_2H$ .

**FRANKLAND, E., AND B. F. DUPPA, 1867.**

J. Chem. Soc. **20**, 102-116; Ann. Chem. **145**, 78-93; Jsb. Chem. 1867, 394.

**Synthetical Researches on Esters. Part II.**

By the action of sodium and then isopropyl iodid on acetic ester, monoisopropyl acetoacetic ester was produced, it is insoluble in water, miscible with ether and alcohol, has a specific gravity of .9804, boils at  $201^{\circ}$  with 758.4 m. m. pressure and distils unchanged. When saponified isopropyl acetone,  $CH_3COCH_2CH(CH_3)_2$ , is produced, it is sparingly soluble in water, miscible with alcohol and ether, boils at  $114^{\circ}$  with 758.4 m. m. pressure and has a specific gravity of .8189 at  $0^{\circ}$ .

The difference is shown between it and two isomers, methyl valeral and ethyl butyral.

**GEUTHER, A., 1869.**

Ztschr. \*Chem. **5**, 27; Bull. Soc. chim. **12**, 377.

**Changing Acetoacetic Ester into Ethylacetic Ester.**

Acetoacetic ester heated to  $120^{\circ}$  with sodethoxid and acetic ester is changed into ethyl acetic acid,  $CH_2C_2H_5CO_2H$ .

\*Original article not consulted.

**WANKLYN, A., 1869.**

Ann. Chem. **149**, 43-49; Jsb. Chem. 1868, 509.

**Research upon Esters.**

The action of sodium in sealed tubes upon a number of esters was investigated and in no case was hydrogen evolved. The esters thus worked with were acetic ester; acetic allyl ester; butyric ester; valeric ester and benzoic ester. The equation for sodium and acetic ester was given as follows:

$3 \text{ C}_2 \text{ H}_3 \text{ O}_2 \text{ C}_2 \text{ H}_5 + 4 \text{ Na} = 3 \text{ Na OC}_2 \text{ H}_5 + \text{Na} (\text{C}_2 \text{ H}_3 \text{ O})_3$ . The author looks upon sodacetoacetic ester as a triacetyl derivative of sodium and upon acetoacetic ester as a triacetyl derivative of hydrogen ; making sodium and hydrogen trivalent.

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**WISLICENUS, J., 1869**

Ann. Chem. **149**, 205-215.

**$\beta$ -Oxybutyric Acid.**

The source of obtaining  $\beta$ -oxybutyric acid is acetoacetic ester which is treated with sodium amalgam and must be kept cool during the reaction for other-wise enough heat is generated by the reaction to decompose the substances into carbonates, acetone and alcohol.

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**WANKLYN, A., 1869.**

Ber. **2**, 64-65 ; Ann. Chem. **150**, 206-208.

**Action of Sodium on Alcohol.**

By the action of sodium on alcohol, sodethoxid was formed, from which the author concludes that sodium is trivalent  $[\text{Na}'''(\text{C}_2 \text{ H}_4)'']'$  OH. This gives rise to a new set of compounds by replacing the hydroxyl hydrogen by radicals.

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**WANKLYN, A., 1869.**

Ber. **2**, 425-427.

**Product of the action of Sodium and then Ethyl Iodid on Acetoacetic Ester.**

No hydrogen is evolved in the first part of this reaction, the chief products of which are sodethoxid and sodacetoacetic ester. Then sodethoxid reacts with acetic ester to form ethyl acetate of sodium,  $\text{CH}_2 (\text{C}_2 \text{ H}_5) \text{ CO}_2 \text{ Na}$ . This reacts with ethyl iodid thus :  $2 \text{ CH}_2 (\text{C}_2 \text{ H}_5) \text{ CO}_2 \text{ Na} + 2 \text{ C}_2 \text{ H}_5 \text{ I} = 2 \text{ Na I} + \text{C}_2 \text{ H}_5 \text{ OH} + \text{C}_6 \text{ H}_8 (\text{C}_2 \text{ H}_5)_2 \text{ O}_3$  and finally  $\text{C}_6 \text{ H}_8 (\text{C}_2 \text{ H}_5)_2 \text{ O}_3$  reacts with sodethoxid to form  $\text{CH}_2 (\text{C}_2 \text{ H}_5) \text{ CO}_2 \text{ Na}$  and butyric ester,  $\text{C}_6 \text{ H}_{12} \text{ O}_2$ .

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**LADENBURG, A., 1870.**

Ber. **3**, 305-306.

**Action of Sodium on Acetic Ester.**

By experimenting on this reaction the author concludes that no hydrogen is given off, and that with perfectly dry acetic ester no action will take place below  $100^\circ$ .

**GEUTHER, A., 1871.**

Ztschr. \*Chem. **7**, 237 ; Bull. Soc. chim. **16**, 107.

**Acetoacetic Ester and Some of its Derivatives.**

When acetoacetic ester is treated with phosphorus pentachlorid, two metameric acids of the formula  $C_4H_6O_2$  are formed, quartenylic and tetracrylic. Chlortetracrylic acid  $C_4H_5ClO_2$ , and its salts are described. Tetrollic acid,  $C_4H_4O_2$ , is formed from chlortetracrylic ester by an excess of alcoholic potash. Ammonia in the cold acts on acetoacetic ester to form a soluble amid,  $C_6H_{11}NO_2$ , and an insoluble amid,  $C_8H_{15}NO_2$ .

\*Original article not consulted.

**MIXTER, WM. G., 1874.**

Ber. **7**, 499-504 ; Bull. Soc. chim. **22**, 279.

**Knowledge of Derivatives of Sodacetic Esters.**

Sodacetoacetic ester was treated with isobutyl iodid and  $C_6H_8(C_4H_9)_2O_3$  was obtained together with some of the mono-butyl derivative,  $C_6H_9(C_4H_9)O_3$ . The dibutyl derivative is colorless, insoluble in water, miscible with alcohol and ether and boils at  $250^\circ$  to  $253^\circ$ .  $C_6H_9(C_4H_9)O_3$  treated with barium hydroxid is saponified to iso-butyl acetone,  $CH_3COCH_2(C_4H_9)$ .

**WISLICENUS, J., 1874.**

Ber. **7**, 683-692 ; J. Chem. Soc. **27**, 883 ; Bull. Soc. chim. **22**, 457.

**Researches on Derivatives of Acetoacetic Ester.**

In regard to the disputed action of sodium on acetic ester the author agrees with Geuther that as final products only sodethoxid and sodacetoacetic ester are produced. By the action of sodium on acetoacetic ester only one hydrogen atom can be replaced, but by replacing that sodium atom by an alkyl group the other hydrogen of the methylene group is rendered replaceable by sodium and then by an alkyl group. The ethyl and diethyl substituted esters were produced and described.

**WISLICENUS, J., RUEGHEIMER, CONRAD, EHRLICH AND ZEIDLER, 1874.**

Ber. **7**, 892-893 ; J. Chem. Soc. **29**, 367 ; Bull. Soc. chim. **23**, 72.

**Derivatives of Acetoacetic Ester.**

Sodacetoacetic ester treated with iodine forms diacetosuccinic ester which melts with decomposition at  $77^\circ$ . Sodacetoacetic ester treated with

monochloroacetic ester forms acetosuccinic ester which boils at  $260^{\circ}$  to  $263^{\circ}$  with partial decomposition, its specific gravity is 1.079 at  $21^{\circ}$ .

Sodacetoacetic ester treated with chloroacetic ester,  $\text{Cl CO}_2 \text{C}_2 \text{H}_5$ , forms aceto-malonic ester which boils at  $238^{\circ}$  to  $240^{\circ}$  and has a specific gravity of 1.080 at  $23^{\circ}$ .

Sodacetoacetic ester treated with allyl iodide forms allylacetoacetic ester an oil with a specific gravity of .982 at  $20^{\circ}$ .

**WISLICENUS, J., ZEIDLER, EHRLICH, ROHRBECK, WALDSCHMIDT, SAUR AND CONRAD, 1875.**

Ber. **8**, 1034-1040; J. Chem. Soc. **29**, 368; Bull. Soc. chim. **25**, 299.

#### Derivatives of Acetoacetic Ester.

Allylacetoacetic ester is saponified to allylacetone,  $\text{CH}_3 \text{CO CH}_2 \text{CH}_2 \text{CH CH}_2$ , which boils at  $130^{\circ}$ . Allylacetoacetic ester when treated with sodethoxid gives allylacetic ester,  $\text{CH}_2 (\text{C}_3 \text{H}_5) \text{CO}_2 \text{C}_2 \text{H}_5$  boiling at  $142^{\circ}$  to  $144^{\circ}$  from which comes allylacetic acid boiling at  $182^{\circ}$ . Benzylacetoacetic ester  $\text{CH}_3 \text{CO CH} (\text{CH}_2 \text{C}_6 \text{H}_5) \text{CO}_2 \text{C}_2 \text{H}_5$  and the dibenzyl derivative are prepared. Methylacetoacetic ester is converted into  $\alpha$ -methyl  $\beta$ -oxybutyric acid and  $\alpha$ -methyl crotonic acid,  $\alpha$ -ethyl  $\beta$ -oxybutyric acid and  $\alpha$ -ethyl crotonic acid are obtained similarly. Ethyl-methyl acetoacetic ester boiling at  $198^{\circ}$  is prepared and from it ethyl-methyl acetic ester boiling at  $132^{\circ}$  and its acid (valeric) boiling at  $137^{\circ}$ .

Dichloro-acetoacetic ester boiling at  $205^{\circ}$  -  $207^{\circ}$  is prepared and from it dichloroacetone. Ethyl acetoacetic ester will form but a mono chlor derivative therefore it is  $\text{CH}_3 \text{CO C Cl} (\text{C}_2 \text{H}_5) \text{CO}_2 \text{R}$  not  $\text{CH}_2 \text{Cl CO CH} (\text{C}_2 \text{H}_5) \text{CO}_2 \text{R}$ .

**WISLICENUS, J., F. CLOWES AND C. HUGGENBERG, 1875.**

Ber. **8**, 1206-1209; J. Chem. Soc. **29**, 565; Bull. Soc. chim. **25**, 460.

#### Ethyl-aceto Succinic Esters.

$\beta$ -Ethyl-acetosuccinic ester was obtained from sodacetoacetic ester and  $\alpha$ -bromobutyric ester. Its formula is

$\text{CH}_3$	$\text{CH}_3$
$\text{CO}$	$\text{CH}_2$
$\text{CH}$	$\text{CH}$
$\text{CO}_2 \text{C}_2 \text{H}_5$	$\text{CO}_2 \text{C}_2 \text{H}_5$

it is a colorless oil, boils at  $262^{\circ}$  and dissolves sodium at ordinary temperatures, giving off hydrogen.  $\alpha$ -ethyl-acetosuccinic ester was obtained

by treating aceto succinic ester with sodium, and the product with ethyl iodid. Its formula is  $\text{CH}_3$

$\text{CO}$

$\text{C} (\text{C}_2 \text{H}_5) - \text{CH}_2$

$\text{CO}_2 \text{C}_2 \text{H}_5 \quad \text{CO}_2 \text{C}_2 \text{H}_5$ , it boils at  $263^\circ$  to  $265^\circ$ ,

and does not dissolve sodium at ordinary temperatures nor when gently heated.

### OPPENHEIM, A., AND H. PRECHT, 1876.

Ber. **9**, 318-323 ; J. Chem. Soc. **30**, 69 ; Jsb. Chem. 1876, 604 ; Bull. Soc. chim. **26**, 355.

#### Formation of Acetoacetic Ester and Oxyuvitic Acid.

After studying the action of sodium on acetic ester the authors conclude that no hydrogen is given off, and that the reaction is as follows:  
 $3 \text{CH}_3 \text{CO}_2 \text{C}_2 \text{H}_5 + 4 \text{Na} = \text{CH}_3 \text{COCHNaCO}_2 \text{C}_2 \text{H}_5 + 3 \text{C}_2 \text{H}_5 \text{ONa}$ .

In reference to oxyuvitic acid, they conclude that it cannot be formed directly from sodacetoacetic ester and chloroform but that the presence of sodium ethoxid is necessary.

### OPPENHEIM, A., AND H. PRECHT, 1876.

Ber. **9**, 323-325 ; J. Chem. Soc. **30**, 69 ; Jsb. Chem. 1876, 572.

#### Production and Properties of Dehydracetic Acid.

Dehydracetic acid was made by passing the vapor of aceto acetic ester through an iron tube heated to dull redness. It is a crystalline substance of the formula  $\text{C}_8 \text{H}_8 \text{O}_4$  which melts at  $108$  and boils at  $269^\circ$ . Acids do not affect it but alkalis decompose it into acetone and acetic acid.

### DEMARCAY, E., 1876.

Compt. rend. **82**, 1337-1339 ; J. Chem. Soc. **30**, 403 ; Ber. **9**, 962 ; Jsb. Chem. 1876, 551 ; Bull. Soc. chim. **27**, 120.

#### Oxypyrotartaric Acid—A Derivative of Acetoacetic Ester.

Acetoacetic ester treated with hydrocyanic acid forms an addition product,  $\text{CH}_3 \text{COH} (\text{CN}) \text{CH}_2 \text{CO}_2 \text{C}_2 \text{H}_5$ , which is decomposed by water, forming oxypyrotartaric acid,  $\text{CH}_3 \text{C} (\text{OH}) (\text{CO}_2 \text{H}) \text{CH}_2 \text{CO}_2 \text{H}$ , ammonia, and alcohol.

### DEMARCAY, E., 1876.

Compt. rend **83**, 449-451 ; J. Chem. Soc. **30**, 506 ; Jsb. Chem. 1876, 569.

#### Research upon the Derivatives of Acetovaleric Ester.

Sodacetoacetic ester and isopropyl iodid,  $\text{CH I} (\text{C}_3 \text{H}_7)_2$ , react to form isopropyl acetoacetic ester,  $\text{CH}_3 \text{COCH} (\text{C}_3 \text{H}_7) \text{CO}_2 \text{C}_2 \text{H}_5$ , which is

acetovaleric ester. It boils at 200 to 202°, colors ferric chlorid rose violet, when treated with bromin and then alcoholic potash and then hydrochloric acid, two acids are formed according to the amount of bromin used. The acids resemble angelic and oxy-angelic acids.

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**EMMERLING, O. AND A. OPPENHEIM, 1876.**

Ber. **9**, 1096-1097 ; Bull. Soc. chim. **27**, 298.

**A New Ester of Acetoacetic Acid.**

Isobutyl-acetoacetic ester was formed which boils at 202° to 206° with some decomposition ; its specific gravity is .979 at 0°. The ester dissolves sodium, and oxyuvitic acid can be made from it.

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**OPPENHEIM, A. AND H. PRECHT, 1876.**

Ber. **9**, 1098 ; Bull. Soc. chim. **27**, 299.

**Action of Anilin on Acetoacetic Ester.**

Acetoacetic ester was treated with anilin in hopes of producing an anilid but diphenyl carbamid  $\text{CO} \begin{cases} \text{NH C}_6\text{H}_5 \\ \text{NH C}_6\text{H}_5 \end{cases}$  melting at 235°, was produced instead.

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**EMMERLING, O. AND A. OPPENHEIM, 1876.**

Ber. **9**, 1098 ; Bull. Soc. chim. **27**, 299.

**Oxidization of Acetoacetic Ester.**

When acetoacetic ester is oxidized by potassium permanganate, potassium acetate, potassium oxalate, alcohol and water are formed.

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**OPPENHEIM, A. AND H. PRECHT, 1876.**

Ber. **9**, 1099-1102 ; Bull. Soc. chim. **27**, 299.

**Dehydracetic Acid.**

Dehydracetic acid boiled with phosphorus trichlorid gives no reaction but when treated with phosphorus oxychlorid and phosphorus penta-

chlorid a compound,  $C_8 H_6 Cl_2 O_2$ , melting at  $101^\circ$  is formed, which proves the presence of the hydroxyl and carboxyl groups, and also that the fourth oxygen atom is united to carbon. Dehydracetic ester,  $C_8 H_7 (C_2 H_5) O_4$ , melts at  $91.6^\circ$ , dehydracetanilid,  $C_8 H_7 (N H C_6 H_5) O_3$ , fuses at  $115^\circ$ , and chlor-dehydracetic acid,  $C_8 H_7 Cl O_4$ , fuses at  $93^\circ$ , brom-dehydracetic acid,  $C_8 H_7 Br O_4$ , was also described. The formula assigned to dehydracetic acid is

$$\begin{array}{c} CH_3 \quad OH \quad CO_2 H \\ CO \quad C = C \\ CH_2 - C = CH \end{array}$$


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### WISLICENUS, J., 1877.

Ann. Chem. **186**, 161-228 ; J. Chem. Soc. **32**, 432.

#### Acetoacetic Ester.

A short review is given of the work done by different chemists on the reaction between sodium and acetoacetic ester. The methylene hydrogen atoms of acetoacetic ester can be replaced by alkyl groups *only* by passing through the mono-sodium, mono-alkyl, and sodium-alkyl compounds, in that order. Diethyl acetoacetic ester boils at  $218^\circ$  and is not attacked by sodium even at  $100^\circ$ . In the reaction between sodium and acetic ester, sodium acetoacetic ester and sodethoxid are formed, and if ethyl iodid be added now, ethyl-acetoacetic ester is formed, upon some of which sodethoxid will instantly act and form sodethylacetoacetic ester, which, in contact with ethyl iodid now gives diethylacetoacetic ester. Frankland and Duppa wrongly attribute the last named body to the first action of sodium on acetic ester. These complications are due to not removing sodethoxid before adding ethyl iodid. The saponification of acetoacetic ester derivatives yields either substituted ketones and a carbonate, or substituted acetates and alcohol.

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### CONRAD, M., 1877.

Ann. Chem. **186**, 228-232 ; J. Chem. Soc. **32**, 435 ; Jsb. Chem.

1877, 689.

#### Acetoacetic Amyl Ester

Amyl acetate treated with sodium produces acetoacetic amyl ester,  $CH_3 CO CH_2 CO_2 C_5 H_{11}$ , with no evolution of hydrogen if cold, and



only slight evolution in a warm reaction. Amyl alcohol is also produced. Acetoacetic amyl ester is colorless, boils at  $223^{\circ}$ , has a specific gravity of .954 at  $10^{\circ}$ , and colors ferric chlorid red. Ethylacetoacetic amyl ester,  $\text{CH}_3 \text{ CO CH (C}_2 \text{ H}_5 \text{) CO}_2 \text{ C}_5 \text{ H}_{11}$ , was also produced, it boils at  $233^{\circ}$  to  $236^{\circ}$ , has a specific gravity of .937 at  $26^{\circ}$  and gives no color with ferric chlorid.

### CONRAD, M., 1877.

Ann. Chem. **186**, 232-244; J. Chem. Soc. **32**, 435; Jsb. Chem. 1877, 690.

#### Halogen Substitution Products of Acetoacetic Ester.

When acetoacetic ester is treated with bromin it takes it up and hydrobromic acid is given off, forming the compound  $\text{C}_6 \text{ H}_8 \text{ Br}_4 \text{ O}_3$ . Its specific gravity is 2.32 at  $21^{\circ}$  and it is decomposed upon distillation. Chlorin passed through acetoacetic ester is absorbed, hydrochloric acid is given off, and  $\text{C}_6 \text{ H}_8 \text{ Cl}_2 \text{ O}_3$  is formed, This boils at  $205^{\circ}$  to  $207^{\circ}$  and its specific gravity is 1.293 at  $16^{\circ}$ . To prove the constitution of the last compound it was treated with hydrochloric acid at  $180^{\circ}$ , when dichloracetone,  $\text{CH}_3 \text{ CO CH Cl}_2$ , was formed, and with caustic potash when dichloracetic ester,  $\text{CH Cl}_2 \text{ CO}_2 \text{ C}_2 \text{ H}_5$ , was separated. Ethylacetoacetic ester was treated with chlorin and  $\text{CH}_3 \text{ CO C Cl (C}_2 \text{ H}_5 \text{) CO}_2 \text{ C}_2 \text{ H}_5$  was obtained. The author decides that the dichloracetoacetic ester is  $\text{CH}_3 \text{ CO C Cl}_2 \text{ CO}_2 \text{ C}_2 \text{ H}_5$ . Amyl ester of acetoacetic acid and the amyl ester of ethylacetoacetic acid were treated with chlorin, and dichloracetoacetic amyl ester and ethyl-monochloracetoacetic amyl ester were produced.

### BONNÉ, JULIUS, 1877.

Ann. Chem. **187**, 1-11; J. Chem. Soc. **32**, 437

#### Benzoylacetoacetic Ester.

When benzoyl chlorid acts upon sodacetoacetic ester the two substances combine and sodium chlorid is formed. The compound, benzoylacetoacetic ester,  $\text{CH}_3 \text{ CO CH (CO C}_6 \text{ H}_5 \text{) CO}_2 \text{ C}_2 \text{ H}_5$ , decomposes, upon being distilled, into carbon monoxid, carbon dioxid, benzoic ester and benzoic acid. When treated with caustic potash methyl phenyl ketone,  $\text{CH}_3 \text{ CO C}_6 \text{ H}_5$ , and a little benzoic acid are produced.

**EHRLICH, FRANZ LOUIS, 1877.**

Ann. Chem. **187**, 11-30; J. Chem. Soc. **32**, 438; Jsb. Chem.  
1877, 689.

**Benzylacetoacetic Ester.**

Benzylacetoacetic ester was made by treating sodacetoacetic ester with benzyl chlorid, it is  $\text{CH}_3 \text{CO CH} (\text{CH}_2 \text{C}_6 \text{H}_5) \text{CO}_2 \text{C}_2 \text{H}_5$ , it has a specific gravity of 1.083 at 18.4° and cannot be distilled. When saponified methyl-phenylethyl ketone,  $\text{CH}_3 \text{CO CH}_2 (\text{CH}_2 \text{C}_6 \text{H}_5)$ , is obtained, it boils at 235°-236° and has a specific gravity of .989 at 23.5°. When this ketone is oxidized acetic and benzoic acids, carbon dioxid and water are produced. Dibenzylacetoacetic ester was also produced. The action of nascent hydrogen on benzylacetoacetic ester was found to be analogous to that on acetoacetic ester, that is,  $\alpha$ -benzyl  $\beta$ -oxybutyric ester was produced.

**ZEIDLER, FRANZ, 1877.**

Ann. Chem. **187**, 30-47; J. Chem. Soc. **32**, 437.

**Allyl-acetoacetic Ester.**

Allyl-acetoacetic ester boils at 206° and gives a carmine color with ferric chlorid, its specific gravity is .982 at 20°. When saponified it yields allyl-acetone,  $\text{CH}_3 \text{CO CH}_2 \text{C}_3 \text{H}_5$ , which boils at 128° to 130° and has a specific gravity of .834 at 27°. It is isomeric with mesityl oxid, boiling point 131°-132°; with dumasin boiling point 120°-125°, and with metacetone boiling point 84°-86°. Allyl acetic acid,  $\text{CH}_2 (\text{C}_3 \text{H}_5) \text{CO}_2 \text{H}$ , also obtained from the saponification, when oxidized becomes succinic acid. Nascent hydrogen converts allyl acetoacetic ester into  $\alpha$ -allyl  $\beta$ -oxybutyric acid.

**CONRAD, M., 1877.**

Ann. Chem. **188**, 217-226; J. Chem. Soc. **34**, 137.

**Acetsuccinic Esters and Derivatives.**

Acetsuccinic ester  $\text{CH}_3$

CO

CH—————CH<sub>2</sub>

$\text{CO}_2 \text{C}_2 \text{H}_5$        $\text{CO}_2 \text{C}_2 \text{H}_5$  was obtained from sod-acetoacetic ester and monochlor-acetic ester, it is insoluble in water,

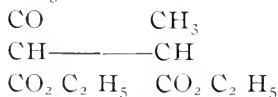
soluble in alcohol, ether and benzene, and boils at  $254^{\circ}$  to  $256^{\circ}$ . When saponified with alcoholic potash, acetic and succinic acids are produced. Barium hydroxid produces  $\beta$ -aceto-propionic acid  $\text{CH}_3 \text{CO CH}_2 \text{CH}_2 \text{CO}_2 \text{H}$ , a crystalline substance which melts at  $31^{\circ}$ . This is probably the same as the levulinic acid of Grote and Tollens (Ann. Chem. **175**, 181). The ethyl ester was also produced.

### CONRAD, M, 1877.

Ann. Chem. **188**, 226-228 ; J. Chem. Soc. **34**, 137.

#### Synthesis of Pyrotartaric Acid from Acetoacetic Ester.

When sodacetoacetic ester is treated with  $\alpha$ -brom-propionic ester,  $\beta$ -methyl-aceto-succinic ester is formed, thus:—  $\text{CH}_3 \text{CO C H Na CO}_2 \text{C}_2 \text{H}_5 + \text{CH}_3 \text{C H Br CO}_2 \text{C}_2 \text{H}_5 = \text{CH}_3$



$\beta$ -Methyl aceto-succinic ester is acted upon by barium hydroxid and the barium salt of pyrotartaric acid is formed.

### ROHRBECK, HERMANN, 1877.

Ann. Chem. **188**, 229-239 ; J. Chem. Soc. **34**, 136.

#### $\alpha$ -Methyl $\beta$ -Oxybutyric Acid and $\alpha$ -Methyl Crotonic Acid.

$\alpha$ -Methyl  $\beta$ -oxybutyric acid was obtained from methyl-acetoacetic ester by the action of sodium amalgam and when heated this  $\alpha$ -methyl  $\beta$ -oxybutyric acid was changed into  $\alpha$ -methyl crotonic acid,  $\text{CH}_3 \text{CH} : \text{C CH}_3 \text{CO}_2 \text{H}$ . The properties and salts of each acid were described.

### WALDSCHMIDT, ERNST, 1877.

Ann. Chem. **188**, 240-248 ; J. Chem. Soc. **34**, 136.

#### Reactions of Acetoacetic Ester.

$\alpha$ -Ethyl  $\beta$ -oxybutyric acid and  $\alpha$ -ethyl-crotonic acid were produced from acetoacetic ester, the reactions being similar to those of Rohrbach\* which proves that they are general. The salts of these two acids were studied and described.

\*See pages 7 and 13.

SAUR, RICHARD, 1877.

Ann. Chem. 188, 257-269.

**Methyl-ethyl-acetoacetic Ester, Methyl-ethyl-acetic Acid and  
 $\alpha$ -Methyl-ethyl- $\beta$ -oxybutyric Acid.**

Methyl-ethyl-acetoacetic ester,  $\text{CH}_3 \text{ CO C}(\text{CH}_3)(\text{C}_2 \text{ H}_5)\text{CO}_2 \text{ C}_2 \text{ H}_5$ , is colorless, boils at  $198^\circ$  and its specific gravity is .974 at  $22^\circ$ . It produces a violet color with ferric chlorid. When treated with sodium ethoxid it gives methyl-ethyl acetic ester,  $\text{CH}(\text{CH}_3)(\text{C}_2 \text{ H}_5) \text{CO}_2 \text{ C}_2 \text{ H}_5$ , while sodium amalgam acting on it produces  $\alpha$ -methyl-ethyl- $\beta$ -oxybutyric ester.

CONRAD, M., 1877.

Ann. Chem. 188, 269-274.

**Metal Acetoacetic Esters.**

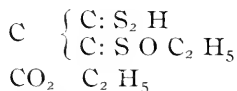
The copper, nickel, cobalt, magnesium, and aluminium salts of acetoacetic ester were produced and described. In each case but one hydrogen atom of the methylene group in acetoacetic ester can be replaced. This can be replaced by either a metal or a non-metal because its position between two carbonyl groups weakens its positive character.

NORTON, TH. AND A. OPPENHEIM, 1877.

Ber. 10, 701-704; Jsb. Chem. 1877, 685.

**Action of Carbon Bisulfid on Acetoacetic Ester.**

By this action a monobasic acid of the formula



was formed which was named by the authors thiorufic acid. A metallic oxid and carbon bisulfid acting on acetoacetic ester produce a compound  $\text{CH}_3 \text{ CO C}(\text{:C: S}) \text{CO}_2 \text{ C}_2 \text{ H}_5$  which the authors consider as the acetyl derivative of  $\text{CH}(\text{:C: S}) \text{CO}_2 \text{ H}$ , which they name thio-carbacetic acid.

**DEMARCAV, E., 1877.**Ber. **10**, 1177-1178.**Acetoacetic Ester.**

The author has worked on the chlorcrotonic acids. The methyl,—ethyl,—and propyl-acetoacetic esters were converted into the corresponding chlorcrotonic acids and described.

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**ROHN, WILHELM, 1877.**Ann. Chem. **190**, 305-322 ; Ber. **11**, 252 ; Jsb. Chem. 1877, 688.**Isobutyl=acetoacetic Ester.....and Isobutyl-acetic Acid.**

Acetoacetic ester treated with isobutyl iodid gives isobutyl acetoacetic ester  $\text{CH}_3$

CO

 $\text{CH CH}_2 \text{CH (CH}_3)_2$  $\text{CO}_2 \text{C}_2 \text{H}_5$ 

which boils at  $217^\circ$ - $218^\circ$  and has a specific gravity of .951 at  $17.5^\circ$ . When saponified it yields isobutyl acetone,  $\text{CH}_3 \text{CO CH}_2 [\text{CH}_2 \text{CH (CH}_3)_2]$ , which boils at  $142^\circ$  to  $144^\circ$  and has a specific gravity of .817 at  $17^\circ$  and isobutyl acetic acid,  $\text{CH}_2 [\text{CH}_2 \text{CH (CH}_3)_2] \text{CO}_2 \text{H}$ .

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**MIEHLE, GUSTAV., 1877.**Ann. Chem. **190**, 322-327 ; J. Chem. Soc. **34**, 490 ; Jsb. Chem.

1877, 688.

**Synthesis of Tricarballic Acid.**

Acetosuccinic ester, made from sodacetoacetic ester and monochloracetic ester, was treated with sodium and then with monochloracetic ester and aceto-tricarballic ester  $\text{CH}_2 \text{CO}_2 \text{C}_2 \text{H}_5$

 $\text{CH}_3 \text{CO-C CO}_2 \text{C}_2 \text{H}_5$  $\text{CH}_2 \text{CO}_2 \text{C}_2 \text{H}_5$  was produced.

It boils, with decomposition at  $280^\circ$  to  $300^\circ$ . When treated with hot potassium hydroxid it gives potassium tricarballic ester from which can be obtained tricarballic acid  $\text{C}_3 \text{H}_5 (\text{CO}_2 \text{H})_3$ .

**DEMARCAÿ, E., 1877.**

Compt. rend. **84**, 554-556 and 1087-1089; J. Chem. Soc. **32**, 590;  
Ber. **10**, 732; Jsb. Chem. 1877, 690.

**Simple Method of Preparing Certain Mono, Di, and Trichlor Acids.**

Phosphoric pentachlorid, acting on a compound of the formula  $\text{CH}_3 \text{CO CH} \times \text{CO}_2 \text{C}_2 \text{H}_5$ , forms a substituted monochlor crotonic ester of the formula  $\text{CH}_2 : \text{C Cl CH} \times \text{CO}_2 \text{C}_2 \text{H}_5$ . In this manner the methyl, ethyl, propyl, isopropyl and allyl crotonic monochlor esters were prepared. Also some di-radical monochlor crotonic esters of the formula  $\text{CH}_2 : \text{C Cl C X Y CO}_2 \text{C}_2 \text{H}_5$  both where X and Y were alkyl radicals and where they were acid radicals. The ethyl-monochlor crotonic ester and its isomer dimethyl-monochlor crotonic ester were prepared and the differences between them noted.

**DEMARCAÿ, E., 1877.**

Compt. rend. **84**, 1032-1033; J. Chem. Soc. **32**, 594.

**Some Derivatives of Acetoacetic Ester.**

By treating ethyl- and methyl-acetoacetic esters each with a quantity of bromin representing one molecule and saponifying the products, two compounds of the composition  $3 \text{C}_5 \text{H}_6 \text{O}_2 + \text{H}_2 \text{O}$  and  $3 \text{C}_4 \text{H}_4 \text{O}_2 + \text{H}_2 \text{O}$  were obtained, which were named *pentic* and *tetric* acids respectively. Just double the amount of bromin being used, two acids were formed each containing one atom of oxygen more. These were named *pentenic* and *tetrenic*. Mono- and di-brom-isopropyl acetoacetic esters also gave rise to two acids, *hexic*,  $3 \text{C}_6 \text{H}_8 \text{O}_2 + \text{H}_2 \text{O}$ , and *hexenic*,  $3 \text{C}_6 \text{H}_8 \text{O}_3 + \text{H}_2 \text{O}$ .

**SCHNAPP, HEINR., 1877.**

Ber. **10**, 1953-1954 and 2227; Ann. Chem. **201**, 62-73; Jsb. Chem. 1877, 718.

**Di-ethyl- $\beta$ -oxybutyric Acid.**

Di-ethyl-acetoacetic ester when treated with sodium amalgam gives diethyl- $\beta$ -oxybutyric acid  $\text{CH}_3 \text{CH}(\text{OH})\text{C}(\text{C}_2 \text{H}_5)_2 \text{CO}_2 \text{H}$ . By heating instead of forming the crotonic acid by splitting off water, it forms acetic aldehyde and di-ethyl-acetic acid. The latter boils at  $195^\circ$  to  $197^\circ$  and has a specific gravity of .945.

**RÜCKER, AUG., 1877.**

Ber. **10**, 1954; Ann. Chem. **201**, 54; J. Chem. Soc. **34**, 292; Jsb. Chem. 1880, 810.

**Methyl Crotonic Acid.**

Methyl-acetoacetic ester,  $\text{CH}_3 \text{ CO CH (CH}_3\text{) CO}_2 \text{ C}_2 \text{ H}_5$ , treated with phosphorus pentachlorid gives only one compound  $\alpha$ -methyl  $\beta$ -chlor crotonic acid  $\text{CH}_2$

C-Cl

CH (CH<sub>3</sub>)

$\text{CO}_2 \text{ H}$  which melts at  $69.5^\circ$ . The barium, sodium and silver salts and the ethyl ester were described.

**WOLFF, CARL, 1877.**

Ber. **10**, 1956-1958; Ann. Chem. **201**, 45; Jsb. Chem. 1877, 687.

**Diallyl-acetoacetic Ester and its Derivatives.**

Diallylacetoacetic Ester,  $\text{CH}_3 \text{ CO C (C}_3 \text{ H}_5\text{)}_2 \text{ CO}_2 \text{ C}_2 \text{ H}_5$ , boils at  $239^\circ$  to  $241^\circ$  and has a specific gravity of .948 at  $25^\circ$ . It is decomposed by alkalis in two ways forming (1) diallylacetone which boils at  $174^\circ$ - $175^\circ$  and (2) into diallylacetic acid which boils at  $221^\circ$ - $222^\circ$  and has a specific gravity of .949 at  $25^\circ$ . To obtain the first product the alkali is added cold and the substance is shaken out with ether. To obtain the second add sulfuric acid to the dry mixture and the acid separates as an oil. The barium, calcium and silver salts are described. Possibly this diallylacetic acid  $\text{C H (C}_3 \text{ H}_5\text{)}_2 \text{ CO}_2 \text{ H}$  when oxidized will give tricarballic acid  $\text{C}_3 \text{ H}_5 (\text{CO}_2 \text{ H})_3$  since allylacetic acid gives succinic acid.

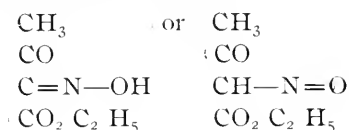
**MEYER, VICTOR, 1877.**

Ber. **10**, 2075-2078; Jsb. Chem. 1877, 518 and 770.

**Azophenylacetoacetic Acid.**

When azobenzene nitrate  $\text{C}_6 \text{ H}_5 \text{ N}_2 \text{ NO}_3$  is treated with potassium acetoacetic ester, azophenylacetoacetic acid  $\text{CH}_3 \text{ CO CH (N}_2 \text{ C}_6 \text{ H}_5\text{)}$

$\text{CO}_2 \text{H}$  is formed, it melts at  $154^\circ$   $155^\circ$ . A new acid,  $\text{C}_6 \text{H}_9 \text{NO}_4$ , was produced by treating acetoacetic ester with nitrous acid, it is so unstable that it cannot be distilled. Its constitution is either




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**WISLICENUS, J., 1877.**

Ber. **10**, 2226-2227.

**The Saponification of Acetoacetic Esters.**

The author calls attention to the double saponification of acetoacetic esters. Substituted acetic esters or acids are obtained as well as substituted ketones.

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**WISLICENUS, J., 1878.**

Ann. Chem. **190**, 257-281 ; J. Chem. Soc. **34**, 402 ; Ber. **11**, 251.

**Decomposition of Acetoacetic Ester by Alkalis.**

A large number of experiments have been performed and tables are given showing the proportions of the different products of saponification under different conditions. It was found that the more concentrated the alkali and the more it was in excess the larger was the proportion of acetic acid and substituted acetic acids and the smaller was the proportion of carbonate and ketones.

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**CONRAD, M., 1878.**

Ber. **11**, 58-60 ; J. Chem. Soc. **34**, 403 ; Jsb. Chem. 1878, 687.

**Action of Sodium on Ethoxyacetic Ester.**

By the action of sodium and then acetic acid on ethoxyacetic ester,  $\text{CH}_2 (\text{O C}_2 \text{H}_5) \text{CO}_2 \text{C}_2 \text{H}_5$ , a compound  $\text{C}_{10} \text{H}_{18} \text{O}_5$  is formed which boils at  $245^\circ$  and is believed to be ethoxyacetyl-ethoxyacetic ester,  $\text{CH}_2 (\text{OC}_2 \text{H}_5) \text{CO CH} (\text{O C}_2 \text{H}_5) \text{CO}_2 \text{C}_2 \text{H}_5$ . It colors ferric chlorid violet, dissolves sodium and forms a barium compound. Heated with an alkali it gives ethoxyacetic ester.

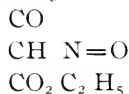


**MEYER, VICTOR AND J. ZÜBLIN, 1878.**

Ber. **11**, 320-324 ; J. Chem. Soc. **34**, 487 ; Jsb. Chem. 1878, 426.

**Nitroso Compounds of Fatty Series. Part I.**

By the action of nitrous acid on acetoacetic ester a compound  $C_6 H_9 NO_4$  was produced. It was liquid even at  $25^\circ$  below zero but after standing some months some of it crystallized. Acetyl chlorid has no action on it which is one proof of the formula



Methyl acetoacetic ester treated with nitrous acid gives nitroso-methyl acetone,  $CH_3 \ CO \ CH \ (CH_3) \ NO$ , which forms white crystals soluble in alcohol, ether and chloroform ; it melts at  $74^\circ$ , and boils at  $185^\circ$   $186^\circ$  undecomposed. It is the first nitroso compound whose vapor density has been determined. Ethyl-acetoacetic ester treated with nitrous acid gives nitroso-ethyl-acetone,  $CH_3 \ CO \ CH \ (C_2 \ H_5) \ NO$ , crystals which are soluble in alcohol, ether and chloroform and slightly soluble in water, it melts at  $53^\circ$ - $55^\circ$ .

**ALLIHN, F., 1878.**

Ber. **11**, 567-570 ; J. Chem. Soc. **34**, 566 ; Jsb. Chem. 1878, 707.

**Action of Sulfuryl Chlorid on Acetoacetic Ester.**

This action produces two compounds according to the proportions of the chlorid used. If an excess of sulfuryl chlorid act upon acetoacetic ester,  $CH_3 \ CO \ C \ Cl_2 \ CO_2 \ C_2 \ H_5$ , is formed. If molecular quantities of the two substances are taken,  $CH_3 \ CO \ C \ HCl \ CO_2 \ C_2 \ H_5$ , is formed which is a colorless liquid boiling at  $193^\circ$  to  $195^\circ$ . Its specific gravity is 1.19 at  $14^\circ$ . When saponified mono-chlor-acetic ester is produced.

**MEYER, VICTOR AND J. ZÜBLIN, 1878.**

Ber. **11**, 692-697 ; J. Chem. Soc. **34**, 659 ; Jsb. Chem. 1878, 726.

**Nitroso Compounds of the Fatty Series. Part II.**

By different manipulations of nitrous acid and methyl-acetoacetic ester three bodies were obtained :—

1) Nitroso-methyl acetone  $\text{CH}_3 \text{CO CH} (\text{CH}_3) (\text{NO})$ ,

2) Nitroso-propionic ester  $\text{CH}_3 \text{CH} (\text{NO}) \text{CO}_2 \text{C}_2 \text{H}_5$ ,

3) Nitroso-propionic acid  $\text{CH}_3 \text{CH} (\text{NO}) \text{CO}_2 \text{H}$ .

Each one was described, as was nitroso acetone,  $\text{CH}_3 \text{CO CH}_2 (\text{NO})$ , also.

### CONRAD, M., 1878.

Ber. II, 1055-1058; J. Chem. Soc. 34, 732; Jsb. Chem. 1878, 743.

#### Synthesis of Phenylated Fatty Acids.

Benzylacetoacetic ester,  $\text{CH}_3 \text{CO CH} (\text{C}_7 \text{H}_7) \text{CO}_2 \text{C}_2 \text{H}_5$ , made from acetoacetic ester, sodium ethoxid and benzyl chlorid is a colorless liquid with boiling point  $276^\circ$  and specific gravity 1.036 at  $15.5^\circ$ . When this is treated with sodium and then with methyl iodid  $\text{CH}_3 \text{CO C} (\text{CH}_3) (\text{C}_7 \text{H}_7) \text{CO}_2 \text{C}_2 \text{H}_5$  is produced. It is colorless, its boiling point is  $287^\circ$  and its specific gravity 1.046 at  $23^\circ$ ; when saponified it yields methyl benzyl acetic acid,  $\text{CH} (\text{CH}_3) (\text{C}_7 \text{H}_7) \text{CO}_2 \text{H}$ . Methyl benzyl acetic benzyl ester or methyl-hydrocinnamein, ethyl benzyl acetoacetic ester,  $\text{CH}_3 \text{CO C} (\text{C}_2 \text{H}_5) (\text{C}_7 \text{H}_7) \text{CO}_2 \text{C}_2 \text{H}_5$ ; and benzyl acetosuccinic ester  $\text{CH}_3$

$\text{CO}$

$\text{C} (\text{C}_7 \text{H}_7) \text{---CH}_2$

$\text{CO}_2 \text{C}_2 \text{H}_5 \quad \text{CO}_2 \text{C}_2 \text{H}_5$  were prepared and described.

### WISLICENUS, J. AND L. LIMPACH, 1878.

Ann. Chem. 192, 128-135; J. Chem. Soc. 34, 783; Ber. II, 1245;

Jsb. Chem. 1878, 720.

#### Synthesis of Glutaric (Pyrotartaric) and $\alpha$ -Methyl Glutaric Acids.

When sodacetoacetic ester is treated with  $\beta$ -iodio-propionic ester,  $\text{CH}_2 \text{I CH}_2 \text{CO}_2 \text{C}_2 \text{H}_5$ , aceto-glutaric ester,  $\text{CH}_3$

$\text{CO}$

$\text{CH---CH}_2 \text{CH}_2 \text{CO}_2 \text{C}_2 \text{H}_5$ ,

$\text{CO}_2 \text{C}_2 \text{H}_5$  is produced.

It is a colorless oil boiling at  $271^{\circ}$ - $272^{\circ}$ , it has a specific gravity of 1.0505 at  $14.1^{\circ}$ . Treating this with alcoholic potash and then sulfuric acid, glutaric acid,  $\text{CH}_2 \text{CO}_2 \text{H}$



$\text{CH}_2 \text{CO}_2 \text{H}$ , is produced. Methyl-aceto-glutaric ester, formed similarly from sodmethylacetoacetic ester boils at  $280^{\circ}$ - $281^{\circ}$  and has a specific gravity of 1.043 at  $20^{\circ}$ . When this is saponified potassium methyl-glutarate  $\text{CH}(\text{CH}_3) \text{CO}_2 \text{K}$



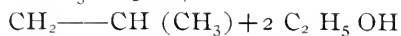
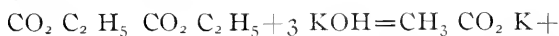
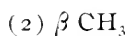
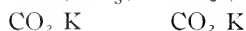
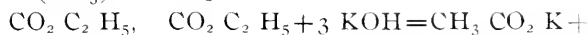
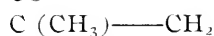
$\text{CH}_2 \text{CO}_2 \text{K}$  is produced which is a crystalline substance melting at  $76^{\circ}$ . The zinc and silver salts were described.

### KRESSNER, G., 1878.

Ann. Chem. **192**, 135-141; J. Chem. Soc, **24**, 783; Ber. **11**, 1245; Jsb. Chem. 1878, 721.

#### Synthesis of Pyrotartaric Acid from $\alpha$ -Methyl-aceto-succinic Ester.

$\alpha$ -Methyl-aceto-succinic ester saponified yields pyrotartaric acid identical with that produced by Conrad, (Ann. Chem. **188**, 226,) from  $\beta$ -methyl-aceto-succinic ester. The two equations are (1)  $\alpha$



**HARDTMUTH, F, 1878.**

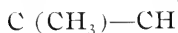
Ann. Chem. **192**, 142-146; J. Chem. Soc. **34**, 782; Ber. **11**, 1245;  
Jsb. Chem. 1878, 726.

 **$\alpha$ - $\beta$ -Dimethyl-acetosuccinic Ester and Symmetrical Dimethyl-succinic Acid.**

$\beta$ -Methyl-acetosuccinic ester  $\text{CH}_3$



is treated with sodium and then with methyl iodid and thus  $\alpha$ - $\beta$ -dimethyl-acetosuccinic ester  $\text{CH}_3$



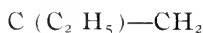
$\text{CO}_2 \text{ R} \quad \text{CO}_2 \text{ R}$  was produced. It boils at  $270^\circ$  to  $272^\circ$  and its specific gravity is 1.057 at  $27^\circ$ . When saponified it gives symmetrical dimethyl succinic acid.  $\text{CH}_3 \quad \text{CH}_3$

**HUGGENBERG, CARL, 1878.**

Ann. Chem. **192**, 146-152; J. Chem. Soc. **34**, 782; Ber. **11**, 1246;  
Jsb. Chem. 1878, 725.

 **$\alpha$ -Ethyl-aceto-succinic Ester and Ethyl-succinic Acid.**

When sodacetosuccinic ester is treated with ethyl iodid  $\alpha$ -ethyl-acetosuccinic ester  $\text{CH}_3$



$\text{CO}_2 \text{ R}$  results. It boils at  $263^\circ$  to  $265^\circ$  and sodium will not act upon it. When this is saponified ethyl-succinic acid is produced which melts at  $98^\circ$ . The barium, calcium and silver salts and ethyl ester of this acid were described.

**CONRAD, M. AND LEONARD LIMPACH, 1878.**

Ann. Chem. **192**, 153-160; Ber. **11**, 1246; J. Chem. Soc. **34**, 781;  
Jsb. Chem. 1878, 706.

**Improved Method of Production of Mono- and Di-organic  
Substituted Acetoacetic Esters.**

Add the ester to a solution of sodium ethoxid made by dissolving sodium in absolute alcohol and then add the alkyl iodid. The products are obtained very free from the byproducts which are formed in the usual methods.

**PRECHT, H., 1878.**

Ber. **11**, 1193-1195; J. Chem. Soc. **34**, 970; Jsb. Chem. 1878, 706.

**Action of Ammonia on Acetoacetic Ester.**

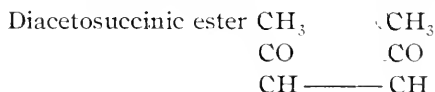
By this action the compound  $C_6H_{11}NO_2$  is formed. It is insoluble in water, soluble in alcohol and ether, and is decomposed by heating. It is probably an amid and is isomeric, not identical with the substance which Geuther obtained and called ammonium ethylene-dimethylene carbonate.\*

\*See pages 1 and 6.

**HARROW, GEO. H. U., 1878.**

J. Chem. Soc. **33**, 425-438; Ann. Chem. **201**, 141; Jsb. Chem. 1878, 731.

**Pyrotritartaric and Carbopyrotritartaric Acids.**



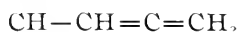
$CO_2 C_2 H_5 CO_2 C_2 H_5$  made from sodacetoacetic ester and iodim, is crystalline and melts at  $78^\circ-79^\circ$ . This treated with dilute sulfuric acid yields the two acids, pyrotritartaric or uvic  $C_7 H_8 O_3$  melting at  $135^\circ-136^\circ$  and carbopyrotritartaric,  $C_8 H_8 O_5$  which melts at  $230^\circ-231^\circ$ . Carbopyrotritartaric acid heated gives pyrotritartaric acid

and carbon dioxid. Carbopyrotritartaric acid fused with potassium hydroxid gives succinic and acetic acids. The formula assigned to carbopyrotritartaric acid is  $\text{CH}_3 \text{ CO CH CO}_2 \text{ H}$



$\text{CO}-\text{O}$ , and the one assigned to

pyrotritartaric acid is  $\text{CH}_3$

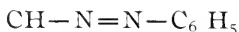


### ZÜBLIN, J., 1878.

Ber. **11**, 1417-1420; J. Chem. Soc. **34**, 879; Jsb. Chem. 1878, 811.

#### Azobenzene=acetoacetic Acid.

This name is proposed for what V. Meyer calls Azo-phenylacetoacetic acid\* (Ber. **10**, 2075.)  $\text{CH}_3$



$\text{CO}_2 \text{ H}$ . The potassium, barium, lead, silver and copper salts and ethyl ester are described and also paraazotoluol-acetoacetic acid,  $\text{CH}_3 \text{ CO CH (N}_2 \text{ C}_6 \text{ H}_4 \text{ CH}_3) \text{ CO}_2 \text{ H}$ , and its ethyl ester.

\*See page 17.

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### BANDROWSKI, E., 1879.

Ber. **12**, 344-346; J. Chem. Soc. **36**, 523; Jsb. Chem. 1879, 628.

#### Behavior of Dibromsuccinic Acid with Water.

At high temperatures water decomposes dibromsuccinic acid by abstracting hydrobromic acid. Two acids are left, one with a boiling point between  $129^\circ$  and  $130^\circ$  which is bromomaleic acid, the other one boils at  $172^\circ$ .

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### HILGER, A., 1879.

Ann. Chem. **195**, 314-317; Ber. **12**, 664; J. Chem. Soc. **36**, 560; Jsb. Chem. 1879, 1081.

#### Detection of Acetoacetic Ester in Urine.

Acetoacetic ester was found in the urine of diabetic patients to the amount of .0399 to .1909 in 100 parts.

**KÖNIG, HEINR., 1879.**

Ber. **12**, 768-770; J. Chem. Soc. **36**, 706; Jsb. Chem. 1879, 662.

**Action of Hydrocyanic and Hydrochloric Acids on Methyl-aceto-acetic Ester.**

Just as these acids act on acetoacetic ester to produce oxypyrotartaric acid so they act on methyl-acetoacetic ester and produce the next higher homologue, oxyadipic acid thus:  $\text{CH}_3 \text{ CO CH (CH}_3\text{) CO}_2 \text{ C}_2 \text{ H}_5 + \text{HCN}=\text{CH}_3 \text{ COH (CN) CH (CH}_3\text{) CO}_2 \text{ C}_2 \text{ H}_5$  and then  $\text{CH}_3 \text{ C OH (CN) CH (CH}_3\text{) CO}_2 \text{ C}_2 \text{ H}_5 + 2 \text{ HCl} + 2 \text{ H}_2 \text{ O} = \text{CH}_3 \text{ COH (CO}_2 \text{ H) CH (CH}_3\text{) CO}_2 \text{ H} + \text{N H}_4 \text{ Cl} + \text{C}_2 \text{ H}_5 \text{ Cl}$ .

**LADENBURG, A. AND L. RÜGHEIMER, 1879.**

Ber. **12**, 953-954; J. Chem. Soc. **36**, 715; Jsb. Chem. 1879, 435.

**Acetoacetic Ester Derivatives of Ortho=tolylendiamin.**

Ortho-tolylendiamin  $\text{C}_6 \text{ H}_3 \text{ CH}_3 (\text{NH}_2)_2$  reacts with acetoacetic ester to form  $\text{C}_6 \text{ H}_3 \text{ CH}_3 < \begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix} > \text{C} < \begin{smallmatrix} \text{CH}_3 \\ \text{CH}_2 \end{smallmatrix} \text{CO}_2 \text{ C}_2 \text{ H}_5$ , a solid, melting at  $82^\circ$ . It is insoluble in water, soluble in alcohol and such solvents; when heated it decomposes into ethenyl-tolylendiamin  $\text{C}_6 \text{ H}_3 \text{ CH}_3 < \begin{smallmatrix} \text{N} \\ \text{NH} \end{smallmatrix} \equiv \text{C} \text{ C H}_3$ , a solid which melts at  $198^\circ$ - $199^\circ$ .

**ALLIHN, F., 1879.**

Ber. **12**, 1298-1300; J. Chem. Soc. **36**, 915; Jsb. Chem. 1879, 627.

**Chlorinated Metal Derivatives of Acetoacetic Ester.**

The chlorinated metal derivatives, corresponding to the formula  $(\text{CH}_3 \text{ CO CCl CO}_2 \text{ C}_2 \text{ H}_5)_x \text{ M}$ , may be produced by shaking the monochlor-acetoacetic ester with an ammoniacal solution of the salt. The copper, magnesium, nickel, and cobalt salts were described. The dichlor-acetoacetic ester will give no metal derivatives.

**JOURDAN, FRIEDRICH, 1879.**

Ann. Chem. **200**, 101-119; J. Chem. Soc. **38**, 313; Jsb. Chem. 1879, 668.

**Mono- and Di-heptyl-acetoacetic Esters.**

Acetoacetic ester treated with heptyl iodid,  $C_7H_{15}I$ , and sodium ethoxid forms heptyl-acetoacetic ester,  $CH_3COCH(C_7H_{15})CO_2C_2H_5$ , a colorless oil which boils at  $271^\circ$  to  $273^\circ$  and has a specific gravity of .9324 at  $17.1^\circ$ . This was saponified and heptyl acetone,  $CH_3COCH_2C_7H_{15}$ , boiling at  $214^\circ$ - $215^\circ$ , with a specific gravity of .829 at  $17.7^\circ$ , and heptyl-acetic acid, identical with nonyl acid, were produced. Diheptyl-acetoacetic ester was made in the similar way, and from this methyl diheptyl carbin ketone (diheptyl acetone),  $CH_3COCH(C_7H_{15})_2$ , and diheptyl acetic acid,  $CH(C_7H_{15})_2CO_2H$ , were produced.

**VENABLE, F. P., 1880.**

Ber. **13**, 1649-1652; Jsb. Chem. 1880, 438.

**Derivatives of Heptanes.**

Heptyl-acetoacetic ester was produced by the Conrad and Limpach method, it boils at  $256^\circ$  to  $260^\circ$ . When saponified it yielded methyl octyl ketone,  $CH_3COCH_2CHCH_3$

$C_5H_{11}$ , which boils at  $196^\circ$  to  $198^\circ$ . This formula was assigned to it because the heptyl bromide,  $C_5H_{11}CHBrCH_3$ , was used to start with.

**MORRIS, GEO. H., 1880.**

J. Chem. Soc. **37**, 6-14; Ber. **13**, 427; Jsb. Chem. 1880, 813.

 **$\alpha$ -Methyl-hydroxy-succinic Acid.**

Acetoacetic ester treated with hydrocyanic acid and then with hydrochloric acid gives,  $CH_3C(OH)CH_2CO_2H$ ,

$CO_2H$  a crystalline substance, soluble in water, alcohol and ether which melts at  $108^\circ$ . It is the same acid as Demareay's oxy-pyrotartaric described in *Compt. rend.* **82**, 1337. The barium, calcium, potassium, silver, lead and copper salts were described. The three isomeric acids of this formula were shortly discussed.



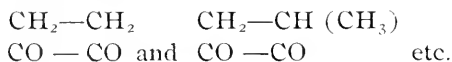
## DEMARCAV, E., 1880.

Bull. Soc. chim. **33**, 516-525 and 575-580 and **34**, 31-37; J. Chem. Soc. **38**, 625.

**Tetric and Oxytetric Acids and their Homologues.**

Methyl-acetoacetic ester when treated with bromin forms two compounds,  $\text{CH}_3 \text{CO C} (\text{CH}_3) \text{Br CO}_2 \text{C}_2 \text{H}_5$  and  $\text{CH}_2 \text{Br CO C} (\text{CH}_3) \text{Br CO}_2 \text{C}_2 \text{H}_5$ . If these are allowed to stand they form  $\text{CH}_3 \text{CO C} (\text{CH}_3) \text{Br H}$  and  $\text{CH}_2 \text{Br CO C} (\text{CH}_3) \text{Br H}$ , but if treated with alcoholic potash they form tetric,  $3 \text{C}_4 \text{H}_4 \text{O}_2 + \text{H}_2 \text{O}$ , and oxytetric acids,  $3 \text{C}_4 \text{H}_4 \text{O}_3 + \text{H}_2 \text{O}$ . Three sets of salts of tetric acid are formed. (1)  $\text{Cu O}$ ,  $\text{C}_4 \text{H}_4 \text{O}_2$ ; (2)  $\text{Ba O}$ ,  $2 \text{C}_4 \text{H}_4 \text{O}_2$ ; (3)  $2 \text{M}_2 \text{O}$ ,  $5 \text{C}_4 \text{H}_4 \text{O}_2$ . Phosphoric pentachlorid with tetric acid forms  $\text{C}_4 \text{H}_4 \text{OCl}_2$  which when treated with chlorin gives  $\text{C}_4 \text{H}_4 \text{Cl}_4 \text{O}$ .

In the above manner, from the alkyl substituted acetoacetic esters, the following acids and many of their salts were produced; pentic,  $3 \text{C}_5 \text{H}_6 \text{O}_2 + \text{H}_2 \text{O}$ ; hexic,  $3 \text{C}_6 \text{H}_8 \text{O}_2 + \text{H}_2 \text{O}$ ; heptic,  $3 \text{C}_7 \text{H}_{10} \text{O}_2 + \text{H}_2 \text{O}$ ; oxyptentic,  $3 \text{C}_5 \text{H}_6 \text{O}_3 + \text{H}_2 \text{O}$ ; oxyhexic,  $3 \text{C}_6 \text{H}_8 \text{O}_3 + \text{H}_2 \text{O}$ ; oxyheptic,  $3 \text{C}_7 \text{H}_{10} \text{O}_3 + \text{H}_2 \text{O}$ , and isohexic and isoxyhexic. The constitution of these was worked out to be;



## HOFMANN, OTTO, 1880.

Ann. Chem. **201**, 73-89; Ber. **13**, 431.

**Action of Zinc and Allyl Iodid on Acetoacetic and Diethyl-acetoacetic Esters.**

The action is the same as with sodium and an alkyl halogen, that is, with acetoacetic ester the mono- and the di-alkyl acetoacetic esters are produced;  $\text{C}_6 \text{H}_9 (\text{C}_3 \text{H}_5) \text{O}_3$  and  $\text{C}_6 \text{H}_8 (\text{C}_3 \text{H}_5)_2 \text{O}_3$ , when allyl iodid is used. When the diallyl acetoacetic ester is treated with zinc and allyl iodid, diallyl acetic ester,  $\text{CH} (\text{C}_3 \text{H}_5)_2 \text{CO}_2 \text{C}_2 \text{H}_5$  is produced.

**GUTHZEIT, MAX, 1880.**

Ann. Chem. **204**, 1-14; Ber. **13**, 1983; J. Chem. Soc. **38**, 871; Jsb. Chem. 1880, 827.

**Octylic-acetoacetic Ester and its Derivatives.**

Sodacetoacetic ester treated with octylic iodid,  $C_8H_{17}$  I, gives octylicacetoacetic ester,  $CH_3COCH(C_8H_{17})CO_2C_2H_5$ , which boils at  $280^\circ$  to  $282^\circ$  and has a specific gravity of .9354 at  $18.5^\circ$ . It yields the two usual saponification products, methyl nonyl ketone  $CH_3COCH_2(C_8H_{17})$ , which boils at  $224^\circ$  to  $226^\circ$ , and octylacetic acid  $CH_2(C_8H_{17})CO_2H$  which is capric acid which boils at  $265^\circ$  to  $267^\circ$ . The barium and calcium salts and ethyl ester of this acid were described. Di-octyl-acetoacetic ester is formed by further treatment of the monoctyl derivative with sodium and octyl iodid, it boils at  $340^\circ$  to  $342^\circ$ . This upon saponification gives dioctylacetone, boiling at  $325^\circ$  to  $330^\circ$  and dioctylacetic or isostearic acid which melts at  $37^\circ$ - $38^\circ$  and boils at  $270^\circ$  to  $275^\circ$  under 100 m. m. pressure. The barium and silver salts and ethyl ester were described.

**BÖCKING, EDUARD, 1880.**

Ann. Chem. **204**, 14-26; Ber. **13**, 1983; J. Chem. Soc. **38**, 872. Jsb. Chem. 1880, 812.

**Two New Syntheses of Ethyl-methyl-oxy-acetic Acid.**

(1) From ethyl-methyl ketone,  $C_2H_5COCH_3$ , by treating it with hydrocyanic acid and then with hydrochloric acid,  $C(C_2H_5)(CH_3)(OH)CO_2H$ , is produced.

(2) From ethyl-methyl-acetic acid (active valeric) which was obtained from ethyl-methyl-acetoacetic ester by saponification.  $CH(C_2H_5)(CH_3)CO_2H$  boils at  $170^\circ$  to  $175^\circ$ , when treated with bromin,  $\alpha$  brom-ethyl-methyl-acetic acid is produced and this with water gives ethyl-methyl-oxy-acetic acid,  $C(C_2H_5)(CH_3)(OH)CO_2H$ .

**WISLICENUS, J., 1880.**

Ann. Chem. **206**, 308-313; J. Chem. Soc. **40**, 409; Ber. **14**, 843; Jsb. Chem. 1881, 502; Bull. Soc. chim. **36**, 657.

**Decomposition of Polybasic Acetoacetic Esters by Alkalis.**

By a great number of experiments it was found that the proportion of ketone or ketonic acid and carbonate increased with the dilution of the alkali and the proportion of acetates or substituted acetates increased with the concentration of the alkali; also that isomers do not give the same proportions of like products.

**BISCHOFF, CARL, 1880.**

Ann. Chem. **206**, 313-337; J. Chem. Soc. **40**, 412; Jsb. Chem. 1881, 744; Ber. **14**, 844.

**Two Homologues of Aceto=propionic Acid.**

$\beta$ -Aceto-isobutyric or  $\alpha$ -methyl-aceto-propionic acid,  $\text{CH}_3 \text{CO CH}_2 \text{CH} (\text{CH}_3) \text{CO}_2 \text{H}$ , and  $\beta$ -aceto-butyric acid,  $\text{CH}_3 \text{CH} (\text{COCH}_3) \text{CH}_2 \text{CO}_2 \text{H}$ , were described together with their production and their salts.

**CLAISEN, L., 1881.**

Ber. **14**, 345-349; J. Chem. Soc. **40**, 405; Jsb. Chem. 1881, 580; Bull. Soc. chim. **36**, 357.

**Condensation of Aldehyde with Acetoacetic Ester.**

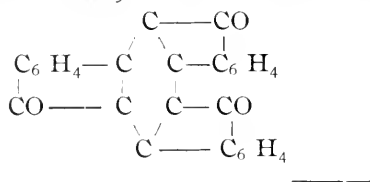
The condensation is effected by passing hydrochloric acid gas through a mixture of the substances. With acetaldehyde, acetethylidenacetic ester,  $\text{CH}_3 \text{CO C} (\text{CH} \text{CH}_3) \text{CO}_2 \text{C}_2 \text{H}_5$ , is produced. It boils at  $210^\circ$  to  $212^\circ$  and will take up two molecules of bromin. Acetobenzylidenacetic ester,  $\text{CH}_3 \text{CO C} (\text{CH} \text{C}_6 \text{H}_5) \text{CO}_2 \text{C}_2 \text{H}_5$ , produced similarly from benzaldehyde boils at  $295^\circ$  to  $297^\circ$ . This also will take up two molecules of bromin.

**GABRIEL, S., 1881.**

Ber. **14**, 919-927 ; J. Chem. Soc. **40**, 733 ; Jsb. Chem. 1881, 798 ;  
Bull. Soc. chim. **36**, 598.

**Condensation Products of Phthalic Anhydrid.**

Acetoacetic ester, phthalic anhydrid,  $C_6H_4(CO)_2O$ , and sodium acetate react together to form ortho-tri-benzoyl-benzene,  $C_{27}H_{12}O_3$ , and a compound,  $C_{12}H_8O_2$ , the composition of which is unknown which boils at 209 to 211. Ortho-tribenzoyl-benzene has the constitution :—

**HANTZSCH, A., 1881.**

Ber. **14**, 1637-1638 ; J. Chem. Soc. **40**, 1028 ; Jsb. Chem. 1881, 586 ;  
Bull. Soc. chim. **36**, 569.

**Condensation Product of Aldehyde-ammonia and Acetoacetic Ester.**

Acetoacetic ester treated with aldehyde-ammonia in presence of zinc chlorid gives  $C_{14}H_{21}NO_4$  which melts at  $131^\circ$  and boils at  $310^\circ$ . Boiled with hydrochloric acid it is entirely decomposed, treated with dry hydrochloric acid gas it gives two bases,  $C_{11}H_{17}NO_2$ , and  $C_8H_{13}N$ . It combines with bromin to form  $C_{14}H_{19}Br_4NO_4$ , and this treated with nitric acid gives  $C_{14}H_{15}Br_4NO_4$ , which melts at  $102^\circ$ .  $C_{14}H_{21}NO_4$  can be oxidized to the base,  $C_{14}H_{19}NO_4$ , which is the ester of collidine-dicarboxylic acid and has the formula  $C_5N(C_2H_5)_3(CO_2C_2H_5)_2$ .

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**DEICHMÜLLER, A., 1881.**

Ann. Chem. **209**, 22-30 ; J. Chem. Soc. **40**, 1162 ; Jsb. Chem. 1881, 1054.

**Diabetic Urine.**

The author decides that the substance in diabetic urine which produces a red color with ferric chlorid is acetoacetic acid, not the ester of that acid because by acidification and distillation acetone but no alcohol is obtained.

**TOLLENS, B., 1881.**

Ann. Chem. **209**, 30-38 ; J. Chem. Soc. **40**, 1162 ; Jsb. Chem. 1881, 1054.

**Diabetic Urine.**

The author decides that the substance in urine of diabetic patients which gives a red color with ferric chlorid is not acetoacetic ester as is claimed, but the free acid of that ester.

**THORNE, L. T., 1881.**

J. Chem. Soc. **39**, 336-344 ; Ber. **14**, 2238, Jsb. Chem. 1881, 759.

**Products of the Action of Alkalis on  $\beta$ -Ethylaceto=succinic Ester.**

Acetoacetic ester treated with  $\alpha$ -brom-butyric ester gives  $\beta$ -ethyl-aceto-succinic ester,  $\text{CH}_3$   $\text{C}_2 \text{H}_5$

CO

CH——CH

$\text{CO}_2 \text{C}_2 \text{H}_5$   $\text{CO}_2 \text{C}_2 \text{H}_5$ , which boils at  $263^\circ$  and has a specific gravity of 1.064 at  $16^\circ$ . When this is treated with an alkali ethyl-succinic acid is formed which is identical with that produced from  $\alpha$ -ethyl-aceto-succinic ester,  $\text{CH}_3$

CO

C  $\text{C}_2 \text{H}_5$ ——CH<sub>2</sub>

$\text{CO}_2 \text{C}_2 \text{H}_5$   $\text{CO}_2 \text{C}_2 \text{H}_5$ , by Huggenberg (Ann. Chem. **192**, 146.) and also  $\alpha$ -ethyl- $\beta$ -aceto-propionic acid, ( $\text{CH}_3$  CO)  $\text{CH}_2$  CH ( $\text{C}_2 \text{H}_5$ )  $\text{CO}_2 \text{H}$ .

**BURTON, BEVERLY S., 1881.**

Am. Chem. J. **3**, 385-395 ; J. Chem. Soc. **42**, 599 ; Ber. **15**, 949 ; Jsb. Chem. 1882, 653.

**On the Propyl Derivatives and Decomposition Products of Acetoacetic Ester.**

Propyl-acetoacetic ester is a liquid which boils at  $208^\circ$  to  $209^\circ$  and has a specific gravity of .981 at  $0^\circ$ .

Di-propyl-acetoacetic ester boils at  $235^\circ$  to  $236^\circ$  and has a specific gravity of .958 at  $0^\circ$ . Quantitive experiments were made in the saponification of these esters and results were obtained, similar to those of

Wislicenus,\* which are given in a table. Di-propyl-acetic acid boils at  $219.5^{\circ}$  and has a specific gravity of .9215 at  $0^{\circ}$ . Di-propyl-acetone boils at  $173^{\circ}$  to  $174^{\circ}$ . Sodium amalgam acting upon di-propyl-acetoacetic ester failed to produce di-propyl- $\beta$ -oxy-butyric acid as was expected but decomposition resulted.

\*Ann. Chem. 186, 161. See pages 10 and 29.

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### WISLICENUS, J., 1882.

Ann. Chem. 212, 239-250; J. Chem. Soc. 42, 934;

Jsb. Chem. 1882, 370.

### Comparisons of the Combining Energies of the Halogens and Sodium with Different Organic Residues.

Many experiments were performed with acetoacetic esters and the following results formulated :

1) Towards similar organic residues the combining energy of chlorine is greatest and of iodine is the least.

2) Among compounds of the same halogen with isomeric radicals, the primary show the least and the tertiary the greatest combining energy.

3) The combining energy of iodine for alcohol radicals of the same category (primary or secondary) increases with the molecular weight (addition of  $\text{CH}_2$ ) this increase being the reciprocal of the increase of the molecular weight.

4) The combining energy of the halogen is considerably less when the residue is an unsaturated primary alcohol radical (allyl for example) but is considerably increased when the halogen is united to a primary but unsaturated carbon atom (vinyl iodide for example.)

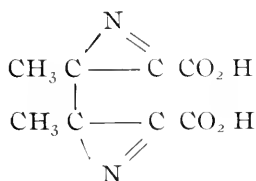
5) A diminution of combining energy is produced by linking of  $\text{CH}_2$  group united with the halogen to carboxyl. The author also shows that the combining energy of the sodium in the sodium-acetoacetic esters is greater than that of the sodium in the sodium-alkyl-acetoacetic esters.

**WLEÜGEL, S., 1882.**

Ber. **15**, 1050-1056; J. Chem. Soc. **42**, 949; Jsb. Chem. 1882, 839;  
Bull. Soc. chim. **38**, 389.

**Upon the Knowledge of Nitroso-acetoacetic Esters.**

Since of the three compounds formed by the treatment of acetoacetic ester with nitrous acid, namely: (1) the nitroso-acetoacetic ester; (2) nitroso-propionic acid and (3) nitroso-acetone, only the second can be reduced to an amid, while the third forms a ketine, the author investigates the action of nascent hydrogen on the first, nitroso-acetoacetic ester, and obtained a dibasic acid which he calls ketindicarboxylic acid,  $C_8H_8N_2O_4$ . The barium, silver, potassium, ammonium and lead salts were described. The author advances the structural formula

**PROPPER, MAX, 1882.**

Ber. **15**, 1154; J. Chem. Soc. **42**, 1193.

**Action of Fuming Nitric Acid on Acetoacetic and on Mono-chlor-acetoacetic Esters.**

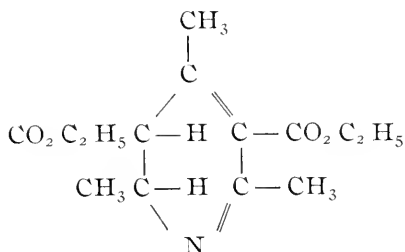
A preliminary notice stating that the author has obtained nitroso-acetic and mono-chlor nitrosoacetic esters by these reactions.

**HANTZSCH, A., 1882.**

Ann. Chem, **215**, 1-82 ; J. Chem. Soc. **44**, 82 ; Ber. **15**, 2912 ; Jsb. Chem. 1882, 491.

**Synthesis of Pyridin Derivatives from Acetoacetic Ester and Aldehyde=Ammonia.**

The condensation product of acetoacetic ester and aldehyde-ammonia is dihydrocollidin-dicarboxylic ester,



The author describes this and many of its derivatives.

**CERESOLE, M., 1882.**

Ber. **15**, 1326-1328 ; J. Chem. Soc. **42**, 1052 ; Jsb. Chem. 1882, 758 ; Bull. Soc. chim. **38**, 390.

**Nitrosoacetone and Acetoacetic Acid.**

By allowing a mixture of acetoacetic ester and potassium hydroxid to stand a day and then treating it with an acid, acetoacetic acid is produced. This is the first production of it. It is a colorless liquid, mixes with water and is strongly acid. It is very unstable, decomposing at less than 100°.

**DUISBERG, C., 1882.**

Ber. **15**, 1378-1388 ; Ann. Chem. **213**, 133-181 ; J. Chem. Soc. **42**, 1192 ; Jsb. Chem. 1882, 841 ; Bull. Soc. chim. **38**, 391.

**Contribution to the Knowledge of Acetoacetic Ester.**

By treating acetoacetic ester with bromin the author cannot get Lippmann's dibrom addition product or Conrad's dibrom addition dibrom



substitution product but gets the five successive substitution products and describes each one. The monobrom product treated with ammonia gives  $C_6H_8O_3$ , the ethyl ester of an acid which the author names oxy-tetrolic. This ester is also produced if sodium act in place of ammonia, and the acid can be obtained by treating the ester with sodium hydroxid. Oxytetrolic acid has just half the molecular formula of Herrmann's succinosuccinic ester (Ann. Chem. **211**, 306). Passing ammonia through acetoacetic ester gives a substance which melts at  $20^\circ$  to  $21^\circ$  which the author calls paramidoacetoacetic ester. Passing hydrochloric acid gas through acetoacetic ester gives a substance  $C_8H_{10}O_3$ , which boils at  $290^\circ$  to  $295^\circ$  and the author calls it carbacetoacetic ester.

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**GOTTSTEIN, L., 1882.**

Ann. Chem. **216**, 29-38; J. Chem. Soc. **44**, 454; Ber. **16**, 403; Jsb. Chem. 1882, 869.

**Two New Caprolactones.**

When acetoacetic ester is treated with  $\alpha$  brom propionic ester;  $\beta$  acetoisobutyric acid can be obtained, and when sodium amalgam acts upon this,  $\alpha$  methyl valero-lactone,  $CH_3CH<\overset{CH_2}{\underset{CO_2}{\text{C}}}>CHCH_3$  is formed.  $\beta$  Methyl valero-lactone,  $CH_2<\overset{CHCH_3}{\underset{CO_2}{\text{C}}}>CHCH_3$ , can be formed in an impure state by the action of sodium amalgam on  $\beta$  acetobutyric acid,  $CH_3CH(C_2H_5O)CH_2CO_2H$ , which is formed from acetosuccinic ester.

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**JAKSCH, R. v., 1882.**

Ber. **15**, 1496; J. Chem. Soc. **42**, 1120; Jsb. Chem. 1882, 1219.

**Occurrence of Acetoacetic Acid in Urine.**

The substance occurring in diseased urine, which gives a red color with ferric chlorid, is proven to be acetoacetic acid.

**HALLER, A. AND A. HELD, 1882.**

Compt. rend. **95**, 235-237; J. Chem. Soc. **42**, 1280; Jsb. Chem. 1882, 845.

**Cyanacetoacetic Ester and its Derivatives.**

Cyanacetoacetic ester,  $\text{CH}_3 \text{CO CH (CN) CO}_2 \text{C}_2 \text{H}_5$ , was produced by passing cyanogen chlorid into sodacetoacetic ester. It is a solid, melts at  $26^\circ$  and remains in a superfused condition even at  $-15^\circ$ ; the liquid has a specific gravity of 1.102 at  $19^\circ$ . Potassium hydroxid decomposes it. The sodium and calcium derivatives were described.

**SCHMID, WILHELM, 1882.**

J. prakt. Chem. **133**, 81-83.

**New Method of Producing Resocyanin.**

Acetoacetic ester and resorcin react in the presence of zinc chlorid to form resocyanin, which is :  $\text{C}_6\text{H}_3(\text{OH})_2\text{C}(\text{CH}_3) : \text{CHCO}_2\text{H}$  [ $\text{C} : \text{OH} : \text{OH} = 1 : 2 : 4$ ].

**WITTENBERG, MAX, 1882.**

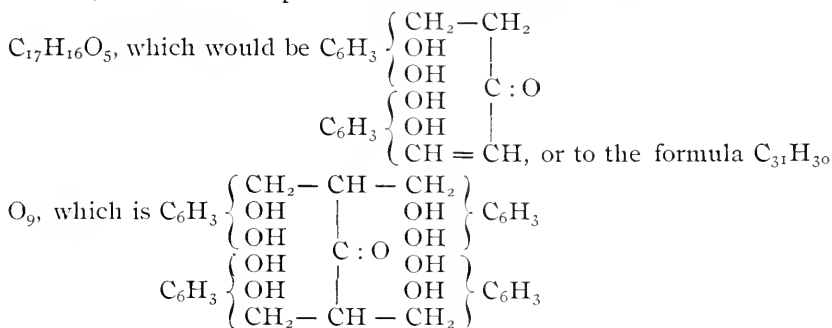
J. prakt. Chem. **134**, 66-78; J. Chem. Soc. **42**, 1289; Ber. **15**, 2908; Jsb. Chem. 1882, 716; Bull. Soc. chim. **39**, 72.

**Resocyanin and the Action of Acetoacetic Ester on Phenols in Presence of Dehydrating Agents.**

Pyrogallol,  $\text{C}_6\text{H}_3(\text{OH})_3$ , and acetoacetic ester react in the presence of sulfuric acid to form allylene-digallein,  $\text{C}_{15}\text{H}_{12}\text{O}_6$ , which melts at  $235^\circ$

and has the constitution :  $\text{C}_6\text{H}_3 \left\{ \begin{array}{l} \text{OH} \\ \text{O}-\text{CH}_2 \\ \text{O} > \text{C} \\ \text{O} > \text{C} \\ \text{O}-\text{CH}_2 \\ \text{OH} \end{array} \right.$  If orcinol,  $\text{C}_6\text{H}_3(\text{CH}_3)(\text{OH})_2$ ,

be used, a substance is produced which answers either to the formula



### CERESOLE, M., 1882.

Ber. **15**, 1871-1878 ; J. Chem. Soc. **44**, 41 ; Jsb. Chem. 1882, 860 ; Bull. Soc. chim. **39**, 35.

### Acetoacetic Acids.

Acetoacetic acid, methyl-, dimethyl- and benzyl-acetoacetic acids were prepared by treating their esters with an alkali in the cold, proving this to be an intermediate action in the ordinary saponification of these esters. The ease with which these compounds decompose, as they do below  $100^\circ$ , is attributed to the position of the carbonyl and carboxyl groups separated by only one methylene or alkyl substituted methylene group.

### CONRAD, M., 1882.

Ber. **15**, 2133-2134 ; J. Chem. Soc. **44**, 177 ; Jsb. Chem. 1882, 845.

### Halogen Substituted Acetoacetic Esters.

The author admits that his formerly described dibrom-acetoacetic dibromid\* is probably only Duisberg's tetrabrom-acetoacetic ester.†

\* See page 11.

† See page 34.

**LIPPMANN, E., 1882.**Ber. **15**, 2142—2144. Jsb. Chem. 1882, 845.**The Position of Bromin in Acetoacetic Ester.**

The author insists upon the correctness of his former statement, which Duisberg denies, that a dibrom-addition dibrom-substitution product of acetoacetic ester,  $C_6H_8Br_2O_3Br_2$ , exists.

**MATTHEWS, A. E. AND W. R. HODKINSON, 1882.**Ber. **15**, 2679; J. Chem. Soc. **44**, 311; Jsb. Chem. 1882, 839.**Production of Acetoacetic Ester.**

Monochlor acetone,  $CH_3COCH_2Cl$ , was treated with potassium cyanid and the cyanid of acetone,  $CH_3COCH_2(CN)$ , was obtained. This, when treated with hydrochloric acid, gave acetoacetic ester.

**YOUNG, SIDNEY, 1882.**Ann. Chem. **216**, 45-52; J. Chem. Soc. **44**, 456; Ber. **16**, 405; Jsb. Chem. 1882, 883.**Peculiar Decomposition of Substituted Acetoacetic Esters.**

When  $\beta$ -ethyl-aceto-succinic ester, 
$$\begin{array}{ccc} CH_3 & & C_2H_5 \\ | & & | \\ CO & & CH \\ | & \text{---} & | \\ CH & & CO_2C_2H_5 \\ | & & | \\ CO_2C_2H_5 & & \end{array}$$
, is heated

it breaks down into ketolactonic ester which can be changed into keto-

lactonic acid, 
$$\begin{array}{ccc} CH_3 & & O \\ | & & || \\ C-O-C & & \\ || & & | \\ C & \text{---} & CHC_2H_5 \\ | & & | \\ CO_2H & & \end{array}, \text{ or } \begin{array}{ccc} CH_2 & & O \\ | & & || \\ C-O-C & & \\ || & & | \\ CH & \text{---} & CHC_2H_5 \\ | & & | \\ CO_2H & & \end{array}$$

JANNY, ALOIS, 1882.

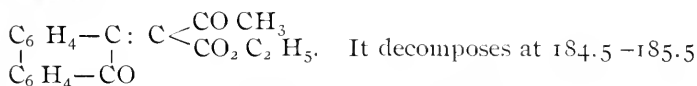
Ber. **15**, 2778-2783.**Acetoxim.**

Near the close of this article the author records having treated acetoacetic ester with hydroxylamin and obtaining a very stable, nitrogenous acid body.

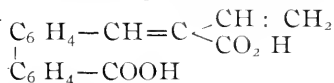
JAPP, FRANCIS R. AND F. W. STREATFEILD, 1883.

J. Chem. Soc. **43**, 27-34.**Condensation Product of Phenanthraquinone with Acetoacetic Ester.**

These substances will condense in presence of either ammonia or an alkali, preferably the latter, to form phenanthroxylene-acetoacetic ester which is:—



It was reduced by hydriodic acid by which the acetyl oxygen was removed giving phenanthroxylene-isocrotonic ester. This was dissolved in an alkali and by adding an acid another substance was produced which was:—



The investigation is being continued.

PROPPER, MAX, 1883.

Ber. **16**, 67; Ann. Chem. **222**, 46; J. Chem. Soc. **44**, 573; Ber. **17**, 14 (c).**Action of Fuming Nitric Acid on Acetoacetic and on Mono=chlor-acetoacetic Esters.**

The author has decided after further study that the two compounds,  $\text{C}_4\text{H}_7\text{O}_3\text{N}$  and  $\text{C}_4\text{H}_6\text{ClO}_3\text{N}$ , obtained by these reactions are oximido bodies,  $\begin{array}{c} \text{CH} : \text{N} \cdot \text{OH} \\ | \\ \text{CO}_2 \text{C}_2\text{H}_5 \end{array}$ , and  $\begin{array}{c} \text{CCl} : \text{N} \cdot \text{OH} \\ | \\ \text{CO}_2 \text{C}_2\text{H}_5 \end{array}$ , not nitroso bodies, as he thought at first. His principal reason for this belief is that no cor-

responding body can be formed from the dichlor-acetoacetic ester as should be the case if it were the monad nitroso group which was introduced.

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**CLAISEN, L. AND F. E. MATTHEWS, 1883.**

Ann. Chem. **218**, 170-185; J. Chem. Soc. **46**, 443; Jsb. Chem. 1883, 963; Bull. Soc. chim. **40**, 473.

**Condensation of Acetoacetic Ester with Aldehydes.**

By treating acetoacetic ester with aldehydes, the following two compounds are formed, the first one much more easily than the second,  $\text{CH}_3\text{CO C}:(\text{:CHR})\text{CO}_2\text{C}_2\text{H}_5$  and  $\text{CH}:(\text{:CHR})\text{COCH}_2\text{CO}_2\text{C}_2\text{H}_5$ . Acet-ethylidenacetic ester,  $\text{CH}_3\text{COC}:(\text{:CHCH}_3)\text{CO}_2\text{C}_2\text{H}_5$ , made by passing hydrochloric acid gas through a mixture of acetoacetic ester and aldehyde is a colorless liquid which boils at  $210^\circ$  to  $212^\circ$ . Its specific gravity is 1.022 at  $15^\circ$ . It easily changes back into aldehyde and acetoacetic ester. The following were prepared and described. Acetisobutylidenacetic ester,  $\text{C}_6\text{H}_8(\text{C}_4\text{H}_8)\text{O}_3$ ; acetisamylidenacetic ester,  $\text{C}_6\text{H}_8(\text{C}_5\text{H}_{10})\text{O}_3$ ; acet-trichlor-ethyliden acetic ester,  $\text{C}_6\text{H}_8(\text{C}_2\text{HCl}_3)\text{O}_3$ , which is  $\alpha$  aceto-trichlor-crotonic ester; aceto-furfural acetic ester,  $\text{C}_6\text{H}_8(\text{C}_5\text{H}_4\text{O})\text{O}_3$ , which is  $\alpha$  acet-furfuracrylic ester; aceto benzal acetic ester  $\text{C}_6\text{H}_8(\text{CHC}_6\text{H}_5)\text{O}_3$ , which is  $\alpha$  acet-cinnamic ester; benzal-acetoethylacetic ester,  $\text{C}_6\text{H}_5\text{CH}:\text{CHCOCH}(\text{C}_2\text{H}_5)\text{CO}_2\text{C}_2\text{H}_5$ ; and benzalacetodiethylacetic ester,  $\text{C}_6\text{H}_5\text{CH}:\text{CHCOC}(\text{C}_2\text{H}_5)_2\text{CO}_2\text{C}_2\text{H}_5$ .

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**DUISBERG, C., 1883.**

Ber. **16**, 133-139; Jsb. Chem. 1883, 1112.

**Converting Acetoacetic Ester into Succinosuccinic Ester which is Convertable into Hydroquinone.**

Succinic ester, made from acetoacetic ester, was treated with sodium and sodium succinosuccinic ester,  $\text{C}_{12}\text{H}_{14}\text{O}_6\text{Na}_2$ , prepared. As in dry acetic ester, the sodium caused no reaction even at  $100^\circ$  until some sodium ethoxid was added. Sodium succinosuccinic ester which has

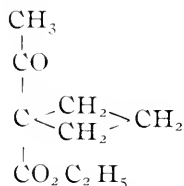
the formula  $\begin{array}{c} \text{CH}_2 - \text{COCHCO}_2 \text{C}_2 \text{H}_5 \\ | \\ \text{CH}_2 - \text{COCHCO}_2 \text{C}_2 \text{H}_5 \end{array}$  melts at  $127^\circ$  and was found to be identical with the substance produced from brom-acetoacetic ester and sodium. This can be changed into hydroquinone,  $\text{C}_6 \text{H}_4 (\text{OH})_2$ , so that these reactions show a case of changing an acid of the fatty series (acetic) into a benzene ring.

**PERKIN, Jr., W. H., 1883.**

Ber. **16**, 208-210; Jsb. Chem. 1883, 1015; Bull. Soc. chim. **40**, 46.

**Action of Trimethylene Bromid on Sod-acetoacetic Ester.**

This reaction gives acetotetramethylene carboxylic ester,



which boils at  $223^\circ$  to  $225^\circ$ . From this the acid and the silver salt of the acid can be obtained.

**DUISBERG, C., 1883.**

Ber. **16**, 295-297; J. Chem. Soc. **44**, 656.

**Addition of Bromin to Acetoacetic Ester.**

This article is a reply to Lippmann and Conrad on this subject. The author declares that acetoacetic ester is saturated and cannot form an addition product.

**CHANCEL, G., 1883.**

Compt. rend. **96**, 1466-1470; J. Chem. Soc. **44**, 914; Jsb. Chem. 1883, 1078; Ber. **16**, 1495.

**New Method of Synthesis of Alkylnitrous Acids.**

Acetoacetic ester and its alkyl derivatives are treated with nitric acid and then with alcoholic potash when the nitrites are formed. Treated

in this manner acetomethyl-acetic ester yields potassium ethyl nitrite,  $\text{CH}_3\text{C}(\text{NO}_2)_2\text{K}$ . Ethyl-acetoacetic ester gives potassium propyl nitrite,  $\text{CH}_3\text{CH}_2\text{C}(\text{NO}_2)_2\text{K}$ . Propyl-acetoacetic ester boils at  $212^\circ$  at 750 <sup>m.m.</sup> pressure and has a specific gravity of .979 at  $0^\circ$ . When treated with nitric acid it gives potassium butyl nitrite,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{NO}_2)_2\text{K}$ . By acidifying the latter butyl nitrous acid is obtained, which boils with some decomposition at  $197^\circ$  and has a specific gravity of 1.205 at  $15^\circ$ .

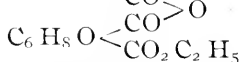
### HANTZSCH, A., 1883.

Ber. 16, 740-742 ; J. Chem. Soc. 44, 1083.

#### Condensation Products of Acetoacetic Esters.

Strong sulfuric acid acting on acetoacetic ester produces (1) mesityl-oxid-di-carboxylic ester,  $\text{C}_6\text{H}_8\text{O} < \begin{smallmatrix} \text{CO}_2 \text{C}_2 \text{H}_5 \\ \text{CO}_2 \text{C}_2 \text{H}_5 \end{smallmatrix}$  (2) mesityl-oxid-anhydro-

dicarboxylic ester,  $\text{C}_6\text{H}_8\text{O} < \begin{smallmatrix} \text{CO}_2 \text{C}_2 \text{H}_5 \\ \text{CO} \end{smallmatrix}$ , and



(3) a crystalline body, polymeric with dehydracetic acid which is a dibasic acid, the formula for which is probably  $\text{C}_{14}\text{H}_{14}\text{O}_7$ ; the name metadehydracetic acid is proposed for it. Ammonia acts on mesityl-

oxid-anhydrodicarboxylic ester to form a salt  $\text{C}_6\text{H}_8\text{O} \text{NH}_3 < \begin{smallmatrix} \text{CO}_2 \text{C}_2 \text{H}_5 \\ \text{CO}_2 \text{N H}_4 \end{smallmatrix}$

which with hydrochloric acid gives  $\text{C}_6\text{H}_8\text{O} < \begin{smallmatrix} \text{CO}_2 \text{C}_2 \text{H}_5 \\ \text{CO}_2 \text{H} \end{smallmatrix}$  which in turn

can be saponified to  $\text{C}_6\text{H}_8\text{O} < \begin{smallmatrix} \text{CO}_2 \text{H} \\ \text{CO}_2 \text{H} \end{smallmatrix}$ .

### CERESOLE, M., 1883.

Ber. 16, 830-832.

#### Diethyl-acetoacetic Acid.

Diethyl-acetoacetic ester is allowed to stand several weeks with a 10% solution of potassium hydroxid, the salt produced is treated with



hydrochloric acid and diethyl-acetoacetic acid,  $\text{CH}_3\text{CO C}(\text{C}_2\text{H}_5)_2\text{CO}_2\text{H}$ , is thus produced. It is very unstable, decomposing at  $60^\circ$  into diethyl-acetone,  $\text{CH}_3\text{CO CH}(\text{C}_2\text{H}_5)_2$ , which boils at  $135^\circ$  to  $137^\circ$ . Diethyl-acetoacetate of sodium was produced.

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**ELION, H., 1883.**

Rec.\* trav. chim. **2**, 33-34 and 202-204 ; Ber. **16**, 1368 and 2762.

**Diacetyl-acetic Ester.**

By treating ethyl-acetoacetic ester with water-free, sodium hydroxid and the product with acetyl chlorid, ethyl-diacetyl-acetic ester was produced, it boils at  $235^\circ$ . Acetoacetic ester treated thus gives diacetyl-acetic ester which boils at  $210^\circ$  to  $213^\circ$  with some decomposition, its specific gravity is 1.1 at  $15^\circ$ . It is decomposed by boiling with water.

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\* Original article not consulted.

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**MATTHEWS, F. E., 1883.**

J. Chem. Soc. **43**, 200-207 ; Ber. **16**, 1372.

**Condensation Products of Aldehydes with Acetoacetic Ester and some Substituted Acetoacetic Esters.**

This article is almost the same as the one by Claisen and Matthews in †Ann. Chem. **218**, 170. The author concludes that all aldehyde condensations with acetoacetic ester take place with the methylene group and are easily accomplished because of the position of the methylene group between the carbonyl and carboxyl groups, but that such condensations with mono-or di-substitution acetoacetic ester take place in the methyl group and consequently are more difficult to accomplish.

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† See page 40.

**PERKIN, Jr., W. H., 1883.**

Ber. **16**, 1787-1789; J. Chem. Soc. **44**, 1083; Jsb. Chem. 1883, 1015.

**Action of Trimethylene Bromid on Acetoacetic, Benzoylacetic  
and Malonic Esters.**

By the action of trimethylene bromid on acetoacetic ester, aceto-tetra-

methylene carboxylic ester,  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CO} \\ | \\ \text{C} < \begin{array}{c} \text{CH}_2 \\ \text{CH}_2 \end{array} > \text{CH}_2 \\ | \\ \text{CO}_2 \text{C}_2 \text{H}_5 \end{array}$ , is formed which is isomeric

but not identical with allyl-acetoacetic ester. From this is obtained aceto-tetramethylene,  $\text{CH}_3 \text{CO CH (CH}_2)_3$ , which boils at 109°-110°

Benzoyl-tetra-methylene carboxylic ester,  $\begin{array}{c} \text{C}_6 \text{H}_5 \\ | \\ \text{CO} \\ | \\ \text{C} < \begin{array}{c} \text{CH}_2 \\ \text{CH}_2 \end{array} > \text{CH}_2 \\ | \\ \text{CO}_2 \text{C}_2 \text{H}_5 \end{array}$ , was formed

from tri-methylene-bromid and benzoyl-acetic ester and from it the acid, the silver salt and benzoyl-tetra-methylene,  $\text{C}_6 \text{H}_5 \text{CO CH (CH}_2)_3$ , were obtained.

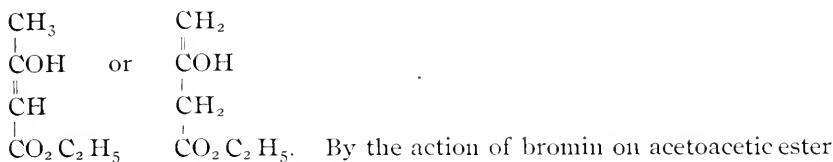
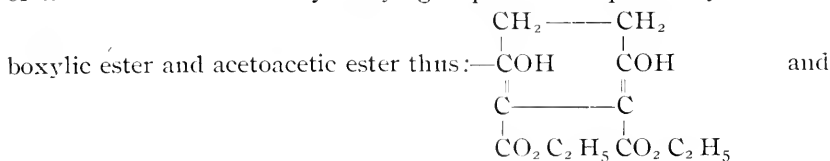
**WEDEL, WILHELM, 1883.**

Ann. Chem. **219**, 71-119; J. Chem. Soc. **46**, 834; Jsb. Chem. 1883, 1060; Bull. Soc. chim. **41**, 181; Ber. **16**, 2288.

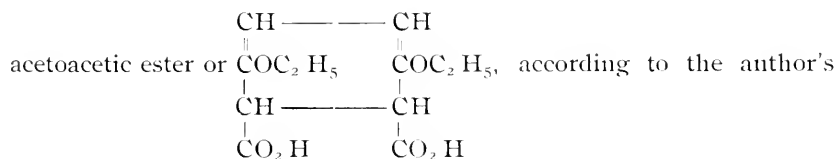
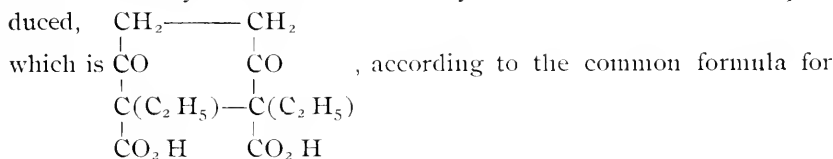
**Derivatives of Acetoacetic Ester.**

By treating dibrom-acetoacetic ester with sodium, an ester,  $\text{C}_6 \text{H}_7 \text{O}_3$ , is produced and from this its acid,  $\text{C}_4 \text{H}_3 \text{O}_3$ . These resemble in properties Duisberg's oxytetrollic acid and ester, but the author decides that the ester is identical with Herrmann's quinon-hydrodicarboxylic ester of the formula  $\text{C}_{12} \text{H}_{14} \text{O}_6$ . By the action of acetyl chlorid on this ester, a diacetyl compound is formed which the author takes as proof

of the existence of the hydroxyl group in both quinon-hydrodicar-



the mono-, di-, and tri-derivatives only could be formed, therefore it was decided that all compounds seeming to have more than three atoms of bromin are mixtures containing some per-brom-acetoacetic ester,  $\text{C}_6 \text{ Br}_{10} \text{ O}_3$ , which was formed and which melts at  $79^\circ$ - $80^\circ$ . By heating mono-brom-ethyl-acetoacetic ester ethyl-succino-succinic acid is produced,



formula. Acetoacetic ester is decomposed by being heated to  $140^\circ$  with acetic acid. Acetyl chlorid decomposes acetoacetic ester and some carbacetoacetic ester is formed, which shows the presence of hydroxyl in acetoacetic ester with which the acetyl chlorid formed hydrochloric acid which produced the carbacetoacetic ester. Glycolic, oxalic and succinic acids decompose acetoacetic ester into carbon dioxid and acetone.

**HANTZSCH, A., 1883.**

Ber. **16**, 1946-1948 ; J. Chem. Soc. **44**, 1082 ; Jsb. Chem. 1883, 1068.

**Condensation of Acetoacetic Methyl Ester with  
Aldehyde=ammonia.**

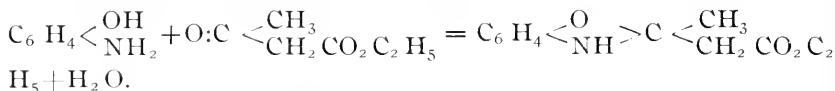
This condensation is entirely similar to that with the ethyl ester, a dihydro-collidin-dicarboxylic methyl ester,  $C_5 N H_2 (CH_3)_3 (CO_2 CH_3)_2$ , being formed. From this were formed dihydro-collidin-monocarboxylic methyl ester,  $C_5 NH_2 (CH_3)_3 H (CO_2 CH_3)$ , and collidin-dicarboxylic methyl ester,  $C_5 N (CH_3)_3 (CO_2 CH_3)_2$ .

**HANTZSCH, A., 1883.**

Ber. **16**, 1948-1952 ; J. Chem. Soc. **44**, 1111 ; Jsb. Chem. 1883, 1069 ;  
Bull. Soc. chim. **42**, 182.

**Condensation of Acetoacetic Ester and Ortho=amidophenol.**

These substances condense as follows :



The product, very unstable, being easily decomposed into its components, melts at 107°-108°. A potassium salt,  $C_{24} H_{29} K O_6 N_2$ , was formed ; one hydrogen atom of the amid group of every two molecules apparently being replaceable.

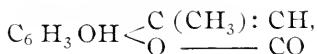
**PECHMANN, H. v. AND C. DUISBERG, 1883.**

Ber. **16**, 2119-2128 ; J. Chem. Soc. **46**, 66 ; Jsb. Chem. 1883, 1065 ;  
Bull. Soc. chim. **42**, 587.

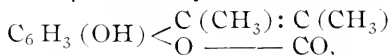
**Compounds of Phenols and Acetoacetic Ester.**

In the presence of a dehydrating agent phenols and acetoacetic ester react to form substituted coumarins.

If resorcin,  $C_6H_4(OH)_2$ , is used  $\beta$ methyl-umbelliferone,



is formed which when treated with potassium hydroxid gives resaceto-phenon,  $C_6H_3(OH)_2COCH_3$ . The methyl ester and the carboxylic acid of  $\beta$ methyl-umbelliferone were formed.  $\alpha$ - $\beta$ -Di-methyl-umbelliferone,



was formed from resorcin and dimethyl-acetoacetic ester. Metatolnene- $\beta$ -methyl-coumarin,  $C_6H_3CH_3 < \underset{O}{\overset{C(CH_3):}{\text{CH}}} \text{CO}$ , was formed from para-cresol,  $C_6H_4OHCH_3$ , and acetoacetic ester.

### PERKIN, Jr., W. H., 1883.

Ber. **16**, 2136-2140 ; J. Chem. Soc. **46**, 64.

#### Action of Ethylene Bromid on Acetoacetic and Benzoyl=acetic Esters.

From acetoacetic ester, ethylene bromid and sodium, aceto-tri-

methylene carboxylic ester,  $\begin{array}{c} CH_3 \\ | \\ CO \\ | \\ C < \begin{array}{l} | \\ CH_2 \\ | \\ CH_2 \\ | \\ CO_2C_2H_5 \end{array} \end{array}$ , is formed, which boils at  $193^\circ$  to

$195^\circ$ . The acid and the silver salt were obtained. Benzoyl-trimethylene carboxylic ester and acid and benzoyl-trimethylene were also produced.

### GEUTHER, A., 1883.

Ann. Chem. **219**, 119-128 ; J. Chem. Soc. **46**, 836 ; Ber. **16**, 2290 ; Jsb. Chem. 1883, 1065.

#### Constitution of Acetoacetic Esters and of Benzene.

The formation of tri-brom-acetoacetic ester by Wedel and the formation of acetoacetic ester from acetic ester are cited as proof of the formula  $CH_3COH : CHCO_2C_2H_5$  and against  $CH_2 : COHCH_2CO_2$

$C_2H_5$ . Attention is called to the colors produced by acetoacetic compounds and phenol compounds with ferric chlorid as indicating by their similarity that these bodies are similarly constituted. Comment is made upon changing the fatty acid into the benzene ring as pointed out by Wedel, that is, acetic ester into acetoacetic ester and this into quinonehydrodicarboxylic ester and this finally into hydroquinone.

**JAKSCH, R. v., 1883.**

\*Ztschr. physiol. Chem. **7**, 487-490. Ber. **16**, 2314.

**Acetoacetic Acid in Urine.**

The author states that he published a paper in 1880 identifying acetoacetic acid in urine, he therefore claims priority to Tollens † (Ber. **14**, 2594).

\* Original article not consulted.

† See page 31.

**KNORR, L., 1883.**

Ber. **16**, 2593-2596; J. Chem. Soc. **46**, 334; Bull. Soc. chim. **42**, 654.

**New Synthesis of Quinolin Derivatives.**

By varied conditions a reaction between acetoacetic ester and anilin is obtained which forms the compound  $CH_3C(NC_6H_5)CH_2CO_2C_2H_5$ , which is very unstable. If the reaction be interrupted by adding sulfuric acid,  $\gamma$  oxy- $\alpha$ -methyl quinolin is obtained, which comes from the compound cited above by its losing alcohol thus:  $CH_3C(NC_6H_5)CH_2CO_2C_2H_5 = C_6H_4 \begin{matrix} N = \\ \diagup \end{matrix} \begin{matrix} CCH_3 \\ | \\ C(OH) \end{matrix} + C_2H_5OH$ . It melts at 222. The intermediate anilin-acetoacetic acid,  $CH_3C(NC_6H_5)CH_2CO_2H$ , was also obtained.

**KNORR, L., 1883.**

Ber. **16**, 2597-2599; J. Chem. Soc. **46**, 302; Jsb. Chem. 1883, 795;  
Bull. Soc. chim. **42**, 655.

**Action of Acetoacetic Ester on Phenylhydrazin.**

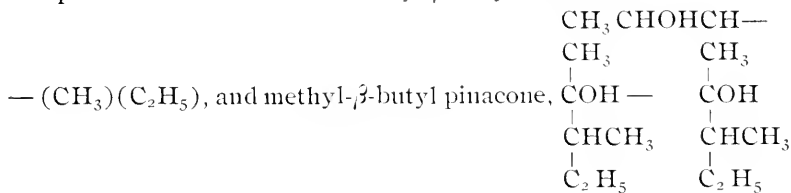
When these substances react there is formed  $\text{CH}_3 \text{C} (\text{HN}_2 \text{C}_6 \text{H}_5) \text{CH}_2 \text{CO}_2 \text{C}_2 \text{H}_5$ . If this be heated on the water bath alcohol is given off and a body  $\text{C}_{10} \text{H}_{10} \text{N}_2 \text{O}$ , is left which melts at  $127^\circ$ ; it resembles carbostyrl; its constitution is unknown. When it is heated with an excess of phenylhydrazin its anhydrid  $\text{C}_{20} \text{H}_{18} \text{N}_4 \text{O}$  is produced, which from its reactions is shown to contain a hydroxyl group.

**WISLICENUS, J., 1883.**

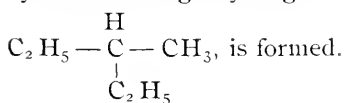
Ann. Chem. **219**, 307-321; J. Chem. Soc. **44**, 966; Jsb. Chem. 1883,  
980.

**Methyl- $\beta$ -butyl Ketone and its Derivatives.**

Ethyl-methyl-acetoacetic ester is saponified and methyl- $\beta$ -butyl ketone,  $\text{CH}_3 \text{COCH} (\text{CH}_3) (\text{C}_2 \text{H}_5)$ , obtained, it boils at  $118^\circ$  and has a specific gravity of .818 at  $14.5^\circ$ . By treating it with sodium and water two products were obtained, methyl- $\beta$ -butyl carbinol,



Methyl- $\beta$ -butyl carbinol is changed into the iodid and then by substituting hydrogen for this iodin methyl-di-ethyl-methane,



**HECKMANN, JACOB, 1883.**

Ann. Chem. **220**, 128-146 ; Ber. **16**, 2675 ; J. Chem. Soc. **46**, 178 ;  
Jsb. Chem. 1883, 1147 ; Bull. Soc. chim. **42**, 54.

**Dinitro=phenyl-acetoacetic Ester.**

By treating sodacetoacetic ester with dinitro-brom-benzene, dinitro-phenyl-acetoacetic ester,  $\text{CH}_3 \text{COCH} [\text{C}_6 \text{H}_3 (\text{NO}_2)_2] \text{CO}_2 \text{C}_2 \text{H}_5$ , is produced, it is crystalline and melts at  $94^\circ$ . From this is produced, by potassium hydroxid, ortho-para-dinitrophenyl acetic acid,  $\text{CH}_2 \text{C}_6 \text{H}_3 (\text{NO}_2)_2 \text{CO}_2 \text{H}$ , which melts at  $160^\circ$  and some di-nitro-toluol,  $\text{C}_6 \text{H}_3 \text{CH}_3 (\text{NO}_2)_2$ . By means of boiling alkalis several complicated decomposition products are obtained  $\text{C}_{24} \text{H}_{18} \text{N}_6 \text{O}_{15}$ , melting at  $105.5^\circ$  and from this,  $\text{C}_{24} \text{H}_{16} \text{K}_2 \text{N}_6 \text{O}_{15}$ ,  $\text{C}_{48} \text{H}_{32} \text{N}_6 \text{O}_{19}$  and a silver salt  $\text{C}_{48} \text{H}_{29} \text{Ag}_3 \text{N}_6 \text{O}_{19}$ .

**PAAL, C., 1883.**

Ber. **16**, 2865-2869 ; J. Chem. Soc. **46**, 598 ; Jsb. Chem. 1883, 1220 ;  
Bull. Soc. chim. **42**, 541.

**Action of Brom=acetophenon on Sodacetoacetic Ester.**

These substances react with separation of sodium bromid to form  $\text{CH}_3 \text{COCH} (\text{CH}_2 \text{COC}_6 \text{H}_5) \text{CO}_2 \text{C}_2 \text{H}_5$ , which easily decomposes into the acid and then into acetophenonacetone,  $(\text{C}_6 \text{H}_5 \text{COCH}_2) \text{CH}_2 \text{COCH}_3$ . When acetophenonacetoacetic ester is boiled with potassium hydroxid an acid  $\text{C}_{12} \text{H}_{10} \text{O}_3$ , is formed by the separation of alcohol and water.

**ROSER, W., 1883.**

Ann. Chem. **220**, 271-278 ; J. Chem. Soc. **46**, 423.

**Isopropyl-succinic or Pimelic Acid.**

Isopropyl-succinic acid was made from acetoacetic ester, monochloroacetic ester and isopropyl iodid, the acetyl being removed and the ester obtained being changed to the acid. This was proven to be identical with pimelic acid  $\text{CH} (\text{CH}_3)_2 - \text{CH} \begin{matrix} \text{CO}_2 \text{H} \\ \text{CH}_2 \text{CO}_2 \text{H} \end{matrix}$ , obtained from camphoric acid.



## WESTENBERGER, BERNHARD, 1883.

Ber. **16**, 2991-2998; J. Chem. Soc. **46**, 581; Jsb. Chem. 1883, 978; Bull. Soc. chim. **42**, 444.

## Isonitroso Bodies.

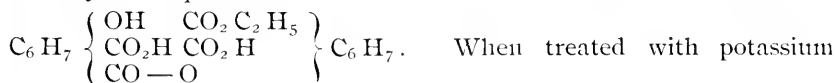
The action of hydroxylamin on acetoacetic ester is given on page 2996 of this article. From this reaction  $\beta$ -isonitroso-butyric ester,  $\text{CH}_3\text{C}(\text{NOH})\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$ , results which is very unstable. The acid is formed from it. Isonitroso-methyl-acetoacetic ester,  $\text{CH}_3\text{C}(\text{NOH})\text{CH}(\text{CH}_3)\text{CO}_2\text{C}_2\text{H}_5$ , and the corresponding ethyl- and diethyl- products were produced from the corresponding substituted acetoacetic esters, proving the reaction to be a general one.

## HANTZSCH, A., 1883.

Ann. Chem. **222**, 1-46; Ber. **17**, 12 (C); Jsb. Chem. 1883, 1070; Bull. Soc. chim. **42**, 502.

## Condensation Products of Acetoacetic Ester.

Acetoacetic ester treated with sulfuric acid gives a condensation product  $\text{C}_{18}\text{H}_{22}\text{O}_9$ , which is formed from four molecules of acetoacetic ester by the separation of three molecules of alcohol. Its formula is



hydroxid and an acid it yields two products, 1)  $\text{C}_6\text{H}_7 \left\{ \begin{array}{l} \text{O} \\ \text{CO} > \\ \text{CO}_2\text{H} \end{array} \right.$ , called mesiten-lactone-carboxylic acid, and 2) its ethyl ester. The radical  $(\text{C}_6\text{H}_9)'$  being designated as mesiten. The mesiten-lactone-carboxylic

acid or isodehydracetic acid has the formula  $\text{CH}_3 - \text{C} : \overset{\text{CO}_2\text{H}}{\underset{\text{O}}{\text{C}}} \cdot \text{C}(\text{CH}_3) : \text{CH}$ ,  
 $\text{O} \text{-----} \text{CO}$

and with potassium hydroxid it yields mesityl oxid. It is a monobasic acid and many of its metallic salts were described. A few complicated salts were investigated which appeared to come from the acid,

$C_6H_7 \begin{cases} OH \\ CO_2H \\ CO_2H \end{cases}$ . Mesiten-lactone,  $C_6H_8 <\overset{O}{CO}>$ , was produced and

described and also oxymesitencarboxylic acid,  $C_6H_8 <\overset{CO_2H}{OH}>$ , and its barium and calcium salts. Mesiten-lactone-carboxylic ester,

$C_6H_7 \begin{cases} O \\ CO> \\ CO_2C_2H_5 \end{cases}$ , or  $CH_3 - C : \overset{\overset{CO_2C_2H_5}{|}}{C} \cdot C(CH_3) : CH$ , is unstable, tends

to take up water, its boiling point is not constant, it boils between  $270^\circ$

and  $310^\circ$ .  $C_6H_6Br \begin{cases} O \\ CO> \\ CO_2C_2H_5 \end{cases}$ , and also  $C_6H_7 \begin{cases} ONH_4 \\ CO_2NH_4 \\ CO_2C_2H_5 \end{cases}$ , were

prepared and described. The latter easily loses ammonia, and when heated with water and hydrochloric acid it gives oxymesitendicarboxylic

acid ester,  $C_6H_7 \begin{cases} OH \\ CO_2H \\ CO_2C_2H_5 \end{cases}$ , which melts at  $76^\circ$  and easily loses

water to form the lactone. It forms salts of the formula  $C_6H_7 \begin{cases} OH \\ CO_2M \\ CO_2C_2H_5 \end{cases}$ ,

of which the copper and lead salts were described. The lactone treated with potassium hydroxid produces homo-mesaconic acid,

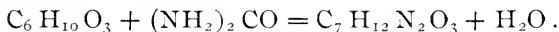
$\overset{\overset{CO_2H}{|}}{H_2C} \cdot C(CH_3) : CH \cdot CO_2H$ , melting at  $147^\circ$ . It forms acid and normal salts, the barium, calcium, copper, silver, acid potassium and acid ammonium salts were described. The author concludes that Duisberg's carbacetoacetic ester,  $C_8H_{10}O_3$ , is identical with his mesiten-lactone-carboxylic ester and also that the hydroxyl group does not exist in acetoacetic ester but that an intermolecular change occurs during condensation, the two acetoacetic ester molecules first lose water and are connected, then an intermolecular change forms a hydroxyl group which gives up its hydrogen to form the lactone. The author thinks the general case to be true that where such a group as  $X_2C : C(OH)X$  occurs it will change into  $X_2CH \cdot COX$  but can change back to the hydroxyl form again during a reaction such as the forming of a lactone.

**BEHREND, ROBERT, 1883.**

Ber. **16**, 3027-3028 ; J. Chem. Soc. **46**, 583.

**Action of Carbamid on Acetoacetic Ester.**

These substances unite thus :



The product formed is crystalline and melts at  $147^\circ$ . Acids decompose it into acetoacetic ester and carbamid again. From it can be obtained the sodium salt of the acid  $\text{C}_5\text{H}_8\text{N}_2\text{O}_3$ , which is  $\text{C}_5\text{H}_7\text{NaN}_2\text{O}_3$ . The author is investigating the structure of the compound.

**JAMES, J. WM., 1884.**

Ann. Chem. **226**, 202-222 ; J. Chem. Soc. **47**, 1-11 ; Ber. **17**, 604 (C).  
Jsb. Chem. 1884, 1120.

**Acetoacetic Ester.**

According to Wedel, ethyl-acetoacetic ester is  $\text{CH}_3\text{COC}_2\text{H}_5:\text{CHCO}_2\text{R}$  and sodiummethylacetoacetic ester would be  $\text{CH}_3\text{CO Na}:\text{C}(\text{C}_2\text{H}_5)\text{CO}_2\text{R}$ , so that if it were treated with acetic acid an isomeric ethylacetoacetic ester should be obtained, but the author proves that an identical ethyl-acetoacetic ester is recovered. Experiments were made to determine if the order of introduction of alkyl radicals in the di-substitution products affects the products. No difference could be detected between allyl-methyl-acetoacetic ester and methyl-allyl-acetoacetic ester or between ethyl-methyl- and methyl-ethyl-acetoacetic esters. Acetyl-acetoacetic ester was produced from acetoacetic ester and acetyl chlorid, it boils at  $200^\circ$ - $205^\circ$  with slight decomposition. It is decomposed by water at ordinary temperatures into acetoacetic ester. The copper and nickel compounds were described. An attempt was made to substitute the hydrogen by sodium but it failed as decomposition took place. The acetyl-methyl-acetoacetic ester was prepared from methyl-acetoacetic ester and acetyl chlorid. Benzoyl-acetoacetic ester,  $\text{CH}_3\text{COCH}(\text{COC}_6\text{H}_5)\text{CO}_2\text{C}_2\text{H}_5$ , and its copper compound were prepared and described.

**JONES, E. J., 1884.**

Ann. Chem. **226**, 287-294; J. Chem. Soc. **48**, 376; Jsb. Chem. 1884, 1188.

**Decomposition of  $\alpha$ -Methyl-propyl- $\beta$ -oxybutyric Acid by Heat.**

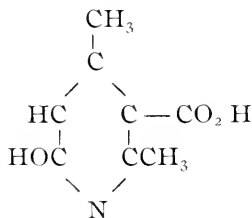
This substance,  $\text{CH}_3\text{CHOHC}(\text{CH}_3)(\text{C}_3\text{H}_7)\text{CO}_2\text{H}$ , is obtained by the action of sodium amalgam on methyl-propyl-acetoacetic ester. Heated to  $170^\circ$  it decomposes into acetaldehyde and methyl-propyl-acetic acid. When methyl-propyl-acetoacetic ester is saponified it yields methyl- $\alpha$ -secondary pentyl ketone,  $\text{CH}_3\text{COCH}(\text{CH}_3)(\text{C}_3\text{H}_7)$ , which boils at  $142^\circ$  to  $147^\circ$  and methyl-propyl-acetic acid which boils at  $193^\circ$ .

**COLLIE, J. NORMAN, 1884.**

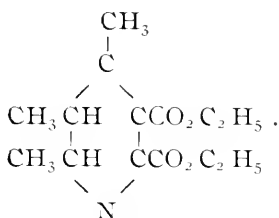
Ann. Chem. **226**, 294-322; J. Chem. Soc. **48**, 373; Ber. **18**, 25 (C); Jsb. Chem. 1884, 1116.

**Action of Ammonia on Acetoacetic Ester.**

Paramido-acetoacetic ester,  $\text{C}_6\text{H}_{11}\text{NO}_2$ , is formed which may be either  $\text{CH}_3\text{C}(\text{NH}_2):\text{CHCO}_2\text{C}_2\text{H}_5$  or  $\text{CH}_3\text{C}(:\text{NH})\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$ . It is easily decomposed into the substances started with. Sodium amalgam changes it into  $\beta$ -oxybutyric acid. It reacts with acetic acid anhydrid to produce  $\beta$ -acetamido- $\alpha$ -crotonic ester,  $\text{CH}_3\text{C}(\text{NHCOCH}_3):\text{CHCO}_2\text{C}_2\text{H}_5$ . When heated it condenses to  $\text{C}_{10}\text{H}_{13}\text{NO}_3$  from which the acid  $\text{C}_8\text{H}_9\text{NO}_3$ , can be produced, which is hydroxylutidin-monocarboxylic acid,



When treated with paraldehyde and sulfuric acid it gives dihydrocollidin dicarboxylic ester,

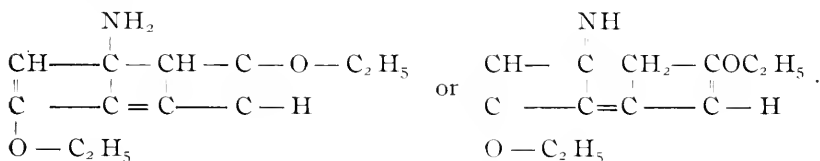


**CANZONERI, F. and G. SPICA, 1884.**

Gazz.\* chim. **14**, 448-453; Ber. **18**, 107 (C); J. Chem. Soc. **48**, 75.

#### Action of Amids on Acetoacetic Ester.

Formamid reacts with acetoacetic ester to form lutidin-mono- and dicarboxylic esters and a compound  $\text{C}_{12}\text{H}_{15}\text{NO}_2$ , to which is attributed the formula



The results of the reaction when acetamid is used will be given later.

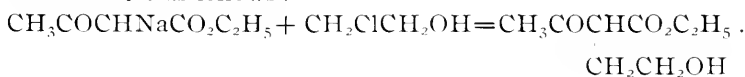
\* Original article not consulted.

**CHANLAROFF, MOEHSIN BEG, 1884.**

Ann. Chem. **226**, 325-343; Ber. **18**, 26 (C); J. Chem. Soc. **48**, 374.

#### Butyrolactone.

This is quite a long article on butyrolactone which is produced from acetoacetic ester as follows:



This substance treated with barium hydroxid and then an acid gives  $\text{CH}_2\text{CO}_2\text{HCH}_2\text{CH}_2\text{OH}$ , which upon heating gives the butyrolactone,  $\text{CH}_2\text{CH}_2$   
 $\begin{array}{c} | \\ \text{CH}_2\text{CO} \end{array} > \text{O}$ .

### ELION, H., 1884.

Rec.\* trav. chim. **3**, 231-270; Ber. **17**, 568 (C).

#### Ethyl-sodacetoacetic Ester and Sodacetoacetic Ester.

Ethyl-sodacetoacetic ester hydrate,  $\text{C}_8\text{H}_{13}\text{NaO}_3 + \text{H}_2\text{O}$ , and sodacetoacetic ester hydrate,  $\text{C}_6\text{H}_9\text{NaO}_3 + \text{H}_2\text{O}$ , were prepared. Sodium bisulfite forms a compound with acetoacetic ester but will form none with diacetyl-, ethylacetyl- and ethyldiacetyl- acetic esters. Ethyl-diacetyl-acetic ester,  $\text{CH}_3\text{COC}(\text{C}_2\text{H}_5)(\text{C}_2\text{H}_3\text{O})\text{CO}_2\text{C}_2\text{H}_5$ , could not be prepared from sodium diacetyl-acetic ester but could be from ethyl-acetoacetic ester and acetyl chlorid.

\*Original article not consulted.

### HELD, A., 1884.

Compt. rend. **98**, 522-525; Bull. Soc. chim. **41**, 330; J. Chem. Soc. **46**, 727; Jsb. Chem. 1884, 1121; Ber. **17**, 204 (C).

#### Ethyl- and Methyl-cyanacetoacetic Esters.

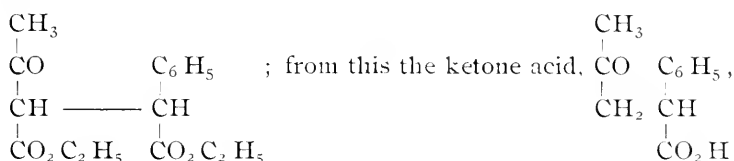
The esters could not be prepared from the cyan-acetoacetic esters but were successfully prepared by treating ethyl-acetoacetic ester and methyl-acetoacetic ester with cyanogen gas. Ethylcyanacetoacetic ester boils at  $105^\circ$ - $110^\circ$  under 15 to 2 m.m. pressure, its specific gravity is .976 at  $20^\circ$ . Methylcyanacetoacetic ester boils at  $90^\circ$ - $95^\circ$  under 15 to 20 m.m. pressure, and has a specific gravity of .996 at  $20^\circ$ . The decomposition products with potassium hydroxid show that the formulæ must be  $\text{CH}_3\text{COC}(\text{CN})(\text{C}_2\text{H}_5)\text{CO}_2\text{C}_2\text{H}_5$  and  $\text{CH}_3\text{COC}(\text{CN})(\text{CH}_3)\text{CO}_2\text{C}_2\text{H}_5$ .

WELTNER, A., 1884.

Ber. **17**, 66-73; J. Chem. Soc. **46**, 746; Jsb. Chem. 1885, 1415; Bull. Soc. chim. **43**, 336.

**Action of Chlor- and Brom-acetone, Aceto-phenon Bromid and Phenyl-brom-acetic Acid on Acetoacetic Ester.**

Chlor- and Brom-acetone act on acetoacetic ester but no definite results were obtained. Aceto-phenon bromid,  $C_6H_5COCH_2Br$ , acting on acetoacetic ester produces aceto-phenon-acetoacetic ester, which, when treated with sodium amalgam becomes a hydroxylactone,  $CH_3CHOHCH<\overset{CH_2}{CO_2}>CHC_6H_5$ . Phenyl-brom-acetic ester and acetoacetic ester produce phenyl-aceto-succinic ester,



is formed, and from this by the action of sodium amalgam the lactone,  $CHC_6H_5CO<\overset{CH_2}{CHCH_3}>O$ , is formed.

CANZONERI, F. and G. SPICA, 1884.

Gazz.\* chim. **14**, 491-492; Ber. **18**, 141 (C); J. Chem. Soc. **48**, 750.

**Acetyl- $\beta$ -imidobutyric Ester.**

By heating acetoacetic ester with acetamid and aluminum chlorid under reduced pressure there is produced acetyl- $\beta$ -imidobutyric ester which melts at  $64^\circ$  to  $65^\circ$ . Its formula is



\*Original article not consulted.

**PERKIN, W. H., 1884.**J. Chem. Soc. **45**, 493 and 540.**Magnetic Rotary Polarization of Compounds in Relation to Chemical Structure.**

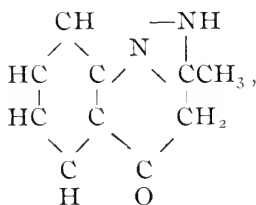
Tables of very many substances are given, among them are :—  
 Acetoacetic ester at  $16.25^\circ$  specific rotation = 0.9278 and molecular rotation = 6.501. Allylacetoacetic ester at  $13.9^\circ$  specific rotation = 1.09022 ; molecular rotation = 10.382.

**KNORR, L., 1884.**

Ber. **17**, 546-552 ; J. Chem. Soc. **46**, 1153 ; Jsb. Chem., 1884, 874 ;  
 Bull. Soc. chim. **43**, 406.

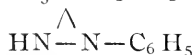
**Action of Acetoacetic Ester on Phenylhydrazin.  
 Quinizin Derivatives.\***

The compound  $C_{10}H_{10}N_2O$ , before described, is now supposed to have the formula

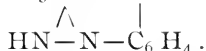


and is named oxymethylquinizin. The reaction between phenylhydrazin and acetoacetic esters is general and consists of two parts :—

(1)  $C_6H_5NHNH_2 + CH_3COCH_2CO_2R = CH_3CCH_2CO_2R$



and (2) this loses alcohol and leaves  $CH_3CCH_2CO$



This substance was studied and a number of its derivatives described, among them were orthotoluoxymethylquinizin, paratoluoxymethylquinizin and  $\beta$ -naphthodimethyloxyquinizin.

\*See page 49.



**PAAL, C., 1884.**

Ber. **17**, 913-918; J. Chem. Soc. **46**, 1177; Bull. Soc. chim. **43**, 626.

**Derivatives of Acetophenon-acetoacetic Ester.**

Acetophenon-acetoacetic ester,  $\begin{array}{c} \text{CH}_3\text{COCHCO}_2\text{C}_2\text{H}_5, \\ | \\ \text{CH}_2\text{COC}_6\text{H}_5 \end{array}$  when saponified yields acetophenonacetone,  $\text{CH}_3\text{COCH}_2(\text{CH}_2\text{COC}_6\text{H}_5)$ , from which were produced two isomeric compounds  $\text{C}_{11}\text{H}_{10}\text{O}$ , one of which melts at  $41^\circ$ - $42^\circ$ , boils at  $235^\circ$  to  $240^\circ$  and yields, on oxidation, benzoic acid. The acid  $\text{C}_{12}\text{H}_{10}\text{O}_3$ , previously described, gives by oxidation benzoic, acetic and carbonic acids. An oil  $\text{C}_{12}\text{H}_9\text{O}_3\text{C}_2\text{H}_5$ , was produced from this acid. The work is being continued.

**LIEBERMANN, C. and S. KLEEMANN, 1884.**

Ber. **17**, 918-921; J. Chem. Soc. **46**, 1120; Jsb. Chem. 1884, 1158; Bull. Soc. chim. **43**, 628.

**Methyl-propyl-acetic Acid.**

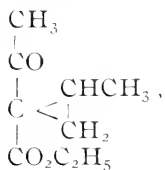
This acid, produced from methyl-propyl-acetoacetic ester which was made from methyl-acetoacetic ester and normal propyl iodid is proven to be identical with the acid of the same name produced from saccharose.

**PERKIN, Jr., W. H., 1884.**

Ber. **17**, 1440-1444; J. Chem. Soc. **46**, 1154; Jsb. Chem. 1884, 1081; Bull. Soc. chim. **44**, 538.

**Trimethylene Derivatives.**

Aceto-methyl-tri-methylene-carboxylic ester,



formed from acetoacetic ester and propylene bromid, boils at  $210^{\circ}$  to  $215^{\circ}$ . From it were produced the free acid and aceto-methyl-trimethylene.

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**PERKIN, Jr., W. H. and C. BERNHART, 1884.**

Ber. **17**, 1522-1527; J. Chem. Soc. **46**, 1121.

**Dehydracetic Acid.**

Dehydracetic acid and hydroxylamin form dehydracetoxim,  $C_7H_8O_3$  CNOH; dehydracetic acid and phenylhydrazin form dehydraceto phenylhydrazin,  $C_8H_8O_3$  NNH  $C_6H_5$ . Monobromdehydracetic acid melting at  $136^{\circ}$ - $137^{\circ}$  was obtained and if this be allowed to stand with alcoholic potash it forms hydroxyl dehydracetic acid,  $C_8H_7O_4OH$ , which melts with decomposition at  $250^{\circ}$  to  $255^{\circ}$ . The silver salt,  $C_8H_6O_5Ag_2$ , was formed showing the acid to be dibasic. By careful treatment of dehydracetic acid with cold potash an oil was obtained which was thought to be acetoacetic acid.

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**RICHTER, V. v. AND H. MÜNZER, 1884.**

Ber. **17**, 1926-1930; J. Chem. Soc. **46**, 1342; Jsb. Chem. 1884, 1051; Bull. Soc. chim. **44**, 242.

**Benzene-azo Ketone.**

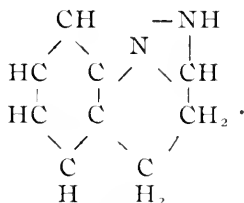
Benzene-azo-acetoacetic ester,  $CH_3COCH(N_2C_6H_5)CO_2C_2H_5$ , formed from acetoacetic ester and diazobenzene chlorid melts at  $75^{\circ}$ . When saponified no substituted acetic acid could be obtained, only the benzene-azo acetone,  $CH_3COCH_2N_2C_6H_5$ , which melts at  $148^{\circ}$ - $149^{\circ}$ . In the same manner para-toluene-azo-acetoacetic ester and para-toluene-azo-acetone were produced.

**KNORR, L., 1884.**

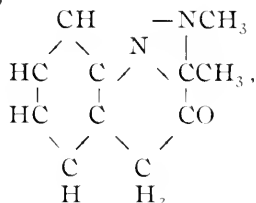
Ber. **17**, 2032-2049; J. Chem. Soc. **46**, 1377; Jsb. Chem. 1884, 877.

**Constitution of Quinizin Derivatives.**

Experiments were made which tend to prove the constitution of these bodies. They probably come from the hypothetical base quinizin, which is :—



Many of the derivatives were described, among them antipyrin, which is dimethyloxyquinizin,



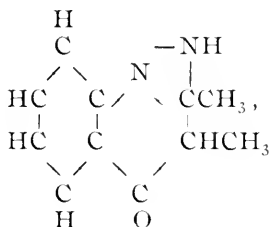
and some of its derivatives.

**KNORR, L. and A. BLANK, 1884.**

Ber. **17**, 2049-2052; J. Chem. Soc. **46**, 1380.

**Action of Substituted Acetoacetic Esters on Phenylhydrazin.**

Methyl-acetoacetic ester and phenylhydrazin form 2':3' dimethyl-oxyquinizin,



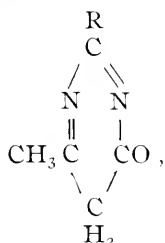
which melts at  $127^{\circ}$  to  $132^{\circ}$ . It is isomeric with antipyrin. Ethyl-acetoacetic ester and phenylhydrazin form 2':3' methyl-ethyl-oxyquinizin which melts at  $108^{\circ}$ .

### PINNER, A., 1884.

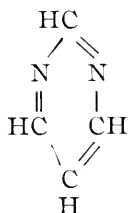
Ber. **17**, 2519-2520; J. Chem. Soc. **48**, 158; Jsb. Chem. 1884, 596.

#### Action of Acetoacetic Ester on Amidins. Part I.

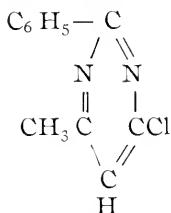
When an amidin of the formula  $R-C \begin{smallmatrix} =NH \\ -NH_2 \end{smallmatrix}$ , acts on acetoacetic ester a compound of the formula



is formed and this compound is changed by phosphorus pentachlorid into the nucleus



Benzamidin gives a compound,  $C_{11}H_{10}N_2O$ , which melts at  $215.5^{\circ}$ - $216^{\circ}$  and gives a platinic chlorid salt. Treated with phosphorus pentachlorid it gives  $C_{11}H_9N_2Cl$ , which is probably



Acetamidin gives  $C_6H_8N_2O$ , which the author is studying.

## PAAL, C., 1884.

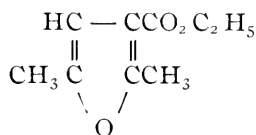
Ber. 17, 2756-2767; J. Chem. Soc. 48, 248.

**Derivatives of Acetophenonacetoacetic Ester and Acetonylacetoacetic Ester.**

One of the two isomeric compounds  $C_{11}H_{10}O$ , obtained by dehydrating acetophenon-acetone is named dehydraceto-phenon-acetone and given one of the three formulæ:  $C_6H_5C:CCH_2COCH_3$ ;  $C_6H_5COCH_2C:CCH_3$ ;  $C_6H_5COCH_2CH_2C:CH$ ; and the other compound is named phenyl-methyl-furfurane,  $\begin{matrix} CH:C(CH_3) \\ CH:C(C_6H_5) \end{matrix} > O$ .

Acetophenon-acetoacetic ester yields analogous dehydrated derivatives.

Acetonyl-acetoacetic ester,  $\begin{matrix} CH_3COCHCO_2C_2H_5 \\ | \\ CH_2COCH_3 \end{matrix}$ , when treated with hydrochloric acid becomes pyrotartaric ester,



A number of other derivatives of the above compounds are described, and their constitution indicated.

## BEHREND, ROBERT, 1884.

Ber. 17, 2846-2847; J. Chem. Soc. 48, 246.

**Derivatives of Carbamid.**

The author is investigating the products of the action of carbamid on acetoacetic ester. From the first compound formed  $C_5H_8N_2O_3$ , are obtained  $C_5H_6N_2O_2$ ;  $C_5H_3N_3O_6$ ;  $C_4H_3N_3O_4$  and  $C_5H_6N_4O_3$ .

PERKIN, Jr., W. H., 1885.

Ber. 18, 218-220; J. Chem. Soc. 48, 515.

**Dehydracetic Acid.**

The subject of the constitution of dehydracetic acid is reviewed and the formula  $\text{CO}_2 \text{HC} \begin{smallmatrix} \text{CO CH} \\ \text{C(CH}_3\text{)}\text{O} \end{smallmatrix} > \text{CCH}_3$ , is advanced. The methyl ester melts at  $90.5^\circ$ , is soluble in water and the solution is decidedly acid. From the methyl ester and sodethoxid the compound  $\text{C}_8\text{H}_6\text{NaCH}_3\text{O}_4$  is formed.

JUST, FEODOR, 1885.

Ber. 18, 319-320; J. Chem. Soc. 48, 513; Ber. 19, 45 (C).

**New Method of Introducing Nitrogenous Radicals in Malonic and Acetoacetic Esters.**

This is by the action of imido-chlorids,—benzanilidimido-chlorid,  $\text{C}_6\text{H}_5\text{Cl}=\text{N}-\text{C}_6\text{H}_5$ , for instance. The chlorine is eliminated and the remaining monad radical is substituted. The author is working in this line.

ALLEN, WM. AND ALFRED KÖLLIKER, 1885.

Ann. Chem. 227, 107-118; J. Chem. Soc. 48, 655; Ber. 18, 154 (C);  
Jsb. Chem. 1885, 768.

**Some derivatives of Triphenyl-carbinyl-bromid.**

When sodacetoacetic ester is treated with triphenyl-carbinyl-bromid,  $\text{CBr}(\text{C}_6\text{H}_5)_3$ , there is produced triphenyl-carbinyl-acetoacetic ester,  $\text{CH}_3\text{CO C}[\text{C}(\text{C}_6\text{H}_5)_3]_2\text{CO}_2\text{C}_2\text{H}_5$ , a substance which melts at  $159.5^\circ$  to

160.5°. When saponified, this yields triphenyl-carbinyl ethel ether,  $C_2H_5OC(C_6H_5)_3$ , melting at 83°, which, treated with acetyl chlorid, gives  $CH_3CO_2C(C_6H_5)_3$ . Triphenyl-carbinyl-acetoacetic ester when distilled yields triphenyl methane,  $CH(C_6H_5)_3$ , which melts at 92° and boils at 358° to 360°.

GEUTHER, A., 1885.

Ann. Chem. **227**, 383-384.

### Upon the History of Acetyl=acetoacetic Esters.

After noticing the claims made by James and by Elion to the first production of these esters, the author calls attention to the fact that Lippmann produced mono- and di- acetyl-acetoacetic esters in 1869 (Ztschr. Chem. 1869, 28).

HAITINGER, L., 1885.

Ber. **18**, 452-453; J. Chem. Soc. **48**, 761.

### Dehydracetic Acid.

Dehydracetic acid when treated with aqueous ammonia gives  $C_8H_9NO_3$  and  $C_7H_9NO$ . The former is an acid which, when heated, gives the latter, which is a weak base. When  $C_7H_9NO$  is distilled with zinc dust lutidin,  $C_7H_9N$ , boiling at 147° to 151° is obtained. Some analogous reactions of dehydracetic acid and chelidonic acid are given. Chelidonic is;  $C(CO_2H) < \begin{smallmatrix} O-C(CO_2H) \\ CH-CO \end{smallmatrix} > CH$  and dehydracetic acid is;  $C(CH_3) < \begin{smallmatrix} O-C(CH_3) \\ CH-CO \end{smallmatrix} > CCO_2H$ .

**BEHREND, ROBERT, 1885.**

Ann. Chem. **229**, 5-31; Ber. **18**, 543 (C); Jsb. Chem. 1885, 654.  
Bull. Soc. chim. **46**, 360.

**Action of Urea on Acetoacetic Ester.**

By this action  $\beta$  Uramidocrotonic ester, 
$$\begin{array}{c} \text{NH} - \text{C} - \text{CH}_3 \\ | \quad | \\ \text{CO} \quad \text{CH} \end{array}$$
, is formed.

$$\begin{array}{c} \text{NH}_2 \quad \text{CO}_2 \text{C}_2 \text{H}_5 \\ | \quad | \\ \text{NH} - \text{C} - \text{CH}_3 \\ | \quad || \\ \text{CO} \quad \text{CH} \\ | \quad | \\ \text{NH} - \text{CO} \end{array}$$
From this was formed methyluracyl, 
$$\begin{array}{c} \text{NH} - \text{C} - \text{CH}_3 \\ | \quad || \\ \text{CO} \quad \text{CH} \\ | \quad | \\ \text{NH} - \text{CO} \end{array}$$
, which decom-

poses at  $270^\circ$ - $280^\circ$  without melting. From this, trimethyluracyl,  $\text{C}_7 \text{H}_{10} \text{N}_2 \text{O}_2$ , melting point  $103^\circ$ ; and nitrouracyl carboxylic acid,  $\text{C}_5 \text{H}_3 \text{N}_3 \text{O}_6$ , were formed, and from the latter, nitrouracyl,  $\text{C}_4 \text{H}_3 \text{N}_3 \text{O}_4$ ; amidouracyl,  $\text{C}_4 \text{H}_5 \text{N}_3 \text{O}_2$ ; and oxyuracyl,  $\text{C}_4 \text{H}_4 \text{N}_2 \text{O}_3$ . Amidouracyl salts give with potassium cyanate, hydroxyxanthin,  $\text{C}_5 \text{H}_6 \text{N}_4 \text{O}_3 + 23 \text{H}_2 \text{O}$ , which may be oxidized to alloxan and this reduced to alloxantin.

**KUCKERT, OTTO, 1885.**

Ber. **18**, 618-620; J. Chem. Soc. **48**, 751; Jsb. 1885, 1351; Bull. Soc. chim. **46**, 8.

**Action of Alkylamins on Acetoacetic Esters.**

Acetoacetic ester when treated with methylamin forms two compounds according to the temperature. If kept at  $0^\circ$  an addition product is formed which melts at  $42^\circ$ - $43^\circ$  and easily changes into an oil, the same as the product which is formed if the temperature is not kept

low. This is either 
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{C} = \text{N} - \text{CH}_3 \\ | \\ \text{CH}_2 \\ | \\ \text{CO}_2 \text{C}_2 \text{H}_5 \end{array}$$
 or 
$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{C} - \text{NHCH}_3 \\ || \\ \text{CH} \\ | \\ \text{CO}_2 \text{C}_2 \text{H}_5 \end{array}$$
. Diethylamin



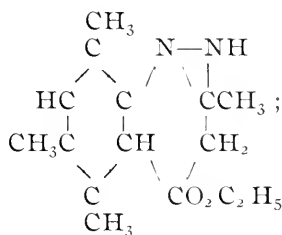
produces the compound of the formula  $\text{C} \begin{array}{c} \text{CH}_3 \\ \vdots \\ \text{CH} \\ \text{CO}_2 \text{C}_2 \text{H}_5 \end{array} \text{N} (\text{C}_2 \text{H}_5)_2$ . The methyl-amin product when treated with paraldehyde and sulfuric acid forms a condensation product  $\text{C}_{15} \text{H}_{23} \text{NO}_4$ , resembling dihydro-collidin dicarboxylic ester.

## HALLER, S., 1885.

Ber. 18, 706-709; J. Chem. Soc. 48, 818; Jsb. Chem. 1885, 1082.

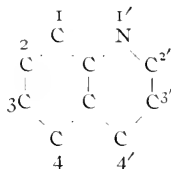
## Trimethyl-quinizin Derivatives.

The following derivatives of acetoacetic ester were described:—pseudo-cumylizinacetoacetic ester,  $\text{C}_{15} \text{H}_{22} \text{O}_2 \text{N}_2$ , which melts at  $77^\circ$ – $78^\circ$  and has the constitution:—



tetramethyl-oxyquinizin,  $\text{C}_9 \text{NH}_3 (\text{CH}_3)_4 \text{ONH}$ ,  $[(\text{CH}_3)_4 = 1:3:4:2']$ ;\*  
 pentamethyl-oxyquinizin (pseudo-cumylantipyrine)  $\text{C}_9 \text{NH}_3 (\text{CH}_3)_4 \text{ONCH}_3$ ,  $[(\text{CH}_3)_3 : \text{NCH}_3 : \text{CH}_3 : \text{O} = 1:3:4:1':2':4']^*$  and isonitrosotetramethyl oxyquinizin,  $\text{C}_{12} \text{H}_{15} \text{O}_2 \text{N}_3$ .

\*The carbon atoms were numbered thus:—

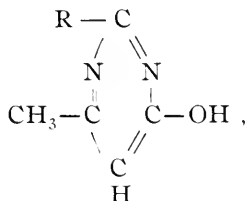


**PINNER, A., 1885.**

Ber. **18**, 759-763; J. Chem. Soc. **48**, 751; Jsb. Chem. 1885, 838;  
Bull. Soc. chim. **45**, 778.

**Action of Acetoacetic Ester on Amidins. Part II.—Pyrimidins.**

The formula



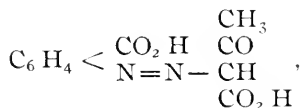
is substituted for that previously assigned to these bodies and the nucleus  $\text{C}_4\text{H}_4\text{N}_2$  is termed pyrimidin. Phenyl-methyl-hydroxy-pyrimidin is further described.

**GRIESS, PETER, 1885.**

Ber. **18**, 960-966; J. Chem. Soc. **48**, 788.

**New Researches upon Diazo Compounds.**

In this article (p. 962) azo-acetoacetic-benzoic acid,



is described. It is produced by treating acetoacetic ester with sulfuric acid and meta diazo-benzoic acid sulphate,  $\text{C}_6\text{H}_4 < \begin{array}{c} \text{CO}_2\text{H} \\ \text{N}=\text{N} - \text{SO}_4\text{H} \end{array}$ .

**SCHILLER-WECHSLER, MAX, 1885.**Ber. **18**, 1037-1052 ; J. Chem. Soc. **48**, 900.**Anilido-pyrotartaric Acid.**

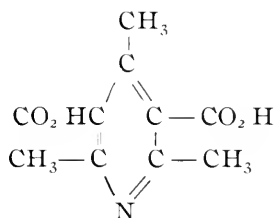
In this article mention is made of cyanhydrin of acetoacetic ester or  $\beta$ -cyan- $\beta$ -oxybutyric ester,  $\text{CH}_3 \text{C} (\text{CN}) (\text{OH}) - \text{CH}_2 \text{CO}_2 \text{C}_2 \text{H}_5$ , which was produced by treating acetoacetic ester with hydrocyanic acid. It is very unstable, from it was prepared  $\beta$ -cyan- $\beta$ -anilido-butyric ester,  $\text{CH}_3 \text{C} (\text{CN}) - (\text{NHC}_6 \text{H}_5) \text{CH}_2 \text{CO}_2 \text{C}_2 \text{H}_5$ , by the action of anilin.

**HANTZSCH, A., 1885.**

Ber. **18**, 1744-1749 ; J. Chem. Soc. **48**, 1078 ; Jsb. Chem. 1885, 815 ;  
Bull. Soc. chim. **46**, 166.

**Constitution of Synthetical Pyridin Derivatives . . . . .**

After discussing the reactions of these bodies the author decides that the tri-methyl-pyridin-dicarboxylic acid obtained from ammonia, aldehyde and acetoacetic ester has the formula :

**MICHAEL, R., 1885.**Ber. **18**, 2020-2029 ; J. Chem. Soc. **48**, 1244 ; Jsb. Chem. 1885, 826.**Synthesis of Pyridin Derivatives from Acetoacetic Ester, Aldehyde and Ammonia.**

By using an excess of aldehyde a product different from the usual one is formed which is  $\alpha - \gamma$ -lutidin- $\beta$ -carboxylic ester,  $\text{C}_5 \text{NH}_2 (\text{CH}_3)_2$

$\text{CO}_2\text{C}_2\text{H}_5$ . It is an oil which boils at  $246^\circ$  to  $247^\circ$  and from it, its acid can be formed, the calcium salt of which, when distilled from lime, yields 2:4, lutidin. The free acid  $\text{C}_5\text{NH}_2(\text{CH}_3)_2\text{CO}_2\text{H}$ , can be oxidized to carbocinchomeric acid,  $\text{C}_5\text{NH}_2(\text{CO}_2\text{H})_3$  [2:3:4], which yields cinchomeric acid,  $\text{C}_5\text{NH}_3(\text{CO}_2\text{H})_2$  [2:3].

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**BUCHKA, K., 1885.**

Ber. 18, 2090-2093; J. Chem. Soc. 48, 1200; Jsb. Chem. 1885, 1351.

**Action of Sulfur Chlorid on Sodacetoacetic Ester.**

The sulfid of acetoacetic ester  $(\text{CH}_3\text{COCHCO}_2\text{C}_2\text{H}_5)_2\text{S}$ , is produced by this action. It melts at  $80^\circ$  to  $81^\circ$ . The reduction or condensation of this was impossible because of its unstability. Carbonyl chlorid acts on sodacetoacetic ester to form chloracetoacetic ester.

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**FITTIG, R., 1885.**

Ber. 18, 2526-2527; J. Chem. Soc. 50, 47.

**Condensation of Acetoacetic Ester with Dibasic Acids.**

Acetoacetic ester condenses with succinic acid to form a compound  $\text{C}_{10}\text{H}_{12}\text{O}_5$ , which melts at  $75^\circ$ - $76^\circ$  and which is a mono-ethyl salt of a dibasic acid,  $\text{C}_8\text{H}_8\text{O}_5$ . This acid melts at  $199^\circ$  to  $200^\circ$ . With sodium pyrotartrate, acetoacetic ester gives the mono-ethyl ester of the acid  $\text{C}_9\text{H}_{10}\text{O}_5$ . Further investigations are being made in this line.

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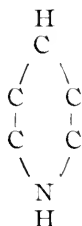
**HANTZSCH, A., 1885.**

Ber. 18, 2579-2586; J. Chem. Soc. 50, 77; Jsb. Chem. 1885, 830.

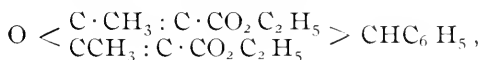
**Constitution of the Synthetical Hydro-pyridin Derivatives.**

The hydrogen in these compounds has been assumed to be in connection with carbon but as Kukart has obtained a substituted hydro-pyridin derivative by the action of paraldehyde and sulfuric acid on the

product of reaction between methyl-amin and acetoacetic ester, it follows that nitrogen must be present as an imido group which gives for the nucleus formula :



Benzylidin-diacetoacetic ester,  $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_9\text{O}_3)_2$ , melting at  $152^\circ$ – $153^\circ$  and dehydrobenzylidin diacetoacetic ester,



melting at  $87^\circ$ – $88^\circ$  were formed from acetoacetic ester and benzaldehyde but the presence of some primary amin is necessary.

**JAKSCH, R. v., 1885.**

Ber. **19**, 781 (C).

#### **Acetonurea and Diaceturea.**

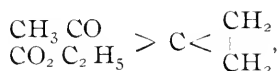
The author states that acetoacetic acid is not found in normal urine and as an explanation of its origin in diseased urine he supposes that it came from acetone by the taking up of oxygen, uniting with formic acid and then splitting off water.

**PERKIN, Jr., W. H., 1885.**

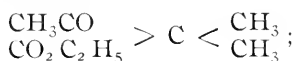
J. Chem. Soc. **47**, 801–855.

#### **Synthetical Formation of Closed Carbon Chains.**

On pages 834–835 of this long article, the author shows the many differences in behavior between acetyl tri-methylene carboxylic ester,



and di-methyl-acetoacetic ester,



although they only differ in composition by two hydrogen atoms.

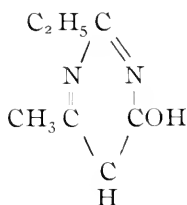
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**PINNER, A., 1885.**

Ber. **18**, 2845-2852 ; J. Chem. Soc. **50**, 45 ; Jsb. Chem. 1885, 840 ;  
Bull. Soc. chim. **45**, 852.

**Action of Acetoacetic Ester on Amidins. Part III.—Pyrimidins.**

With the exception of formamidin all the amidins experimented with form pyrimidins ; formamidin yields cyanacetoacetic ester. Acetamidin yields di-methyl-hydroxy-pyrimidin, propionamidin yields ethyl-methyl-hydroxy-pyrimidin,



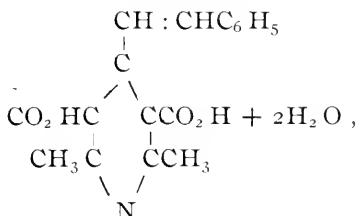
Phenyl-methyl-hydroxy-pyrimidin,  $\text{C}_{11} \text{ H}_{10} \text{ N}_2 \text{ O}$  ; phenyl-methyl-pyrimidin,  $\text{C}_{11} \text{ H}_{10} \text{ N}_2$  ; phenyl-methyl-ethoxy-pyrimidin,  $\text{C}_{11} \text{ H}_9 (\text{OC}_2 \text{ H}_5) \text{ N}_2$  ; and phenyl-methyl-pyrimidin anilid,  $\text{C}_{11} \text{ H}_9 \text{ N}_2 \text{ NHC}_6 \text{ H}_5$  were described.

## EPSTEIN, W., 1885.

Ann. Chem. **231**, 1-36; J. Chem. Soc **50**, 257; Ber. **19**, 18 (C);  
Bull. Soc. chim. **46**, 435.

**Condensation of Cinnamaldehyde with Ammonia and Acetoacetic Ester.**

These substances condense to form benzylidenedihydrocollidin-dicarboxylic ester which melts at  $148^{\circ}$  to  $149^{\circ}$  and which can be oxidized to benzylidene-collidin-dicarboxylic acid,



which melts at  $218^{\circ}$  to  $219^{\circ}$ . When anhydrous it melts at  $241^{\circ}$ . The potassium salt may be oxidized by potassium permanganate to lutidin-tricarboxylic acid which is different from the one described by Hantzsch in Ber. **15**, 2915 and **17**, 2908. By reduction it gives lutidin which is *α-α'*-dimethylpyridine, an isomer of Hantzsch's lutidin.

## ENGELMANN, FRANZ, 1885.

Ann. Chem. **231**, 37-71; Ber. **19**, 16 (C); J. Chem. Soc. **50**, 258; Jsb. Chem. 1885, 1357; Bull. Soc. chim. **46**, 437.

**Action of Homologues of Acetaldehyde on Ammonia and Acetoacetic Ester.**

Hydroparvolin-dicarboxylic ester,  $\text{C}_5\text{NH}_2(\text{CH}_3)_2\text{C}_2\text{H}_5(\text{CO}_2\text{C}_2\text{H}_5)_2$ , is formed from acetoacetic ester, propaldehyde and alcoholic ammonia, it melts at  $110^{\circ}$ . By oxidation it loses its two hydrogen atoms and then by saponification parvolin-dicarboxylic acid,  $\text{C}_5\text{N}(\text{CH}_3)_2\text{C}_2\text{H}_5(\text{CO}_2\text{H})_2$ , is formed which melts at  $289^{\circ}$  to  $290^{\circ}$ . Parvolin,  $\text{C}_5\text{NH}_2(\text{CH}_3)_2\text{C}_2\text{H}_5$ , boils at  $186^{\circ}$  and has a specific gravity of .916 at 14. Hydroisopropyl-lutidindicarboxylic ester,  $\text{C}_5\text{NH}_2(\text{CH}_3)_2\text{C}_3\text{H}_7(\text{CO}_2\text{C}_2\text{H}_5)_2$ , obtained by using isobutylaldehyde melts at  $97^{\circ}$ . From

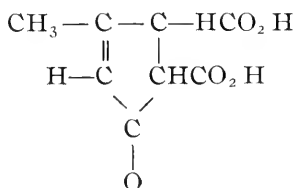
it were obtained lutidin-dicarboxylic ester and acid. Hydroisobutyl-lutidindicarboxylic ester,  $C_5 N (CH_3)_2 C_4 H_9 H_2 (CO_2 C_2 H_5)_2$ , obtained by using valeraldehyde melts at  $100^\circ$ . The mono-ethyl salt and free acid of isobutyl-lutidin dicarboxylic were obtained and also isobutyl-lutidin,  $C_5 N (CH_3)_2 H_2 C_4 H_9$ , a liquid boiling at  $210^\circ$  to  $213^\circ$ .

### FITTIG, R., 1885.

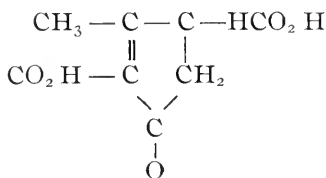
Ber. **18**, 3410-3413; J. Chem. Soc. **50**, 225.

#### Constitution of Carbopyrotritartaric Acid.

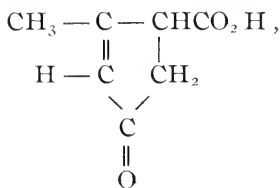
The product of the action of acetoacetic ester and succinic acid,  $C_8 H_8 O_5$ , which is isomeric with carbopyrotritartaric acid is called methronic acid and the two acids are given the following formulæ: Carbopyrotritartaric acid:



Methronic acid:



When heated they both give carbon dioxid and pyrotritartaric acid:





**BAEYER, ADOLF, 1885.**

Ber. **18**, 3454-3460 ; J. Chem. Soc. **50**, 223 ; Jsb. Chem. 1885, 1346 ;  
Bull. Soc. chim. **46**, 440.

**Synthesis of Acetoacetic Ester and Phloroglucin.**

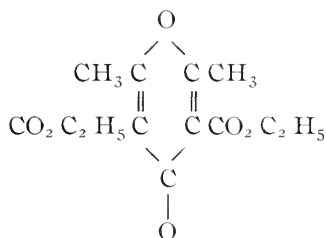
The author discusses the constitution of sodacetoacetic ester, siding with Frankland and Duppa and Wislicenus against Geuther, showing the inconsistencies of the formula  $\text{CH}_3\text{CO Na} : \text{CHCO}_2\text{C}_2\text{H}_5$  and inclining to Frankland and Duppa's view that sodacetic ester is formed as an intermediate product in the action of sodium on acetic ester. Phloroglucin is prepared by treating the product of the action of sodium on malonic ester with caustic potash, and the formula  $\text{CO} < \begin{smallmatrix} \text{CH}_2\text{CO} \\ \text{CH}_2\text{CO} \end{smallmatrix} > \text{CH}_2$  is suggested for it.

**CONRAD, M. AND M. GUTHZEIT, 1886.**

Ber. **19**, 19-26 ; J. Chem. Soc. **50**, 333 ; Jsb. Chem. 1886, 1331.

**Action of Carbonyl Chlorid on Cupracetoacetic Ester.**

Dehydro-diacetyl-acetone-dicarboxylic ester is thus produced. It is a crystalline substance melting at  $79^\circ\text{--}80^\circ$ , and it has the following structural formula :



Acted upon by ammonia this compound gives lutidone-dicarboxylic ester melting at  $221^\circ$ ; by simply substituting NH for the oxygen of the ring. Trimethyl-pyridone-dicarboxylic ester melting at  $193^\circ$  and phenyl-dimethyl-pyridone-dicarboxylic ester melting at  $170^\circ\text{--}171^\circ$  were prepared from the dehydro-compound.

**JAMES, J. WM., 1886.**

J. Chem. Soc. **49**, 50-58 ; Ann. Chem. **231**, 235-244.

**Action of Phosphorus Pentachlorid on Diethyl-acetoacetic Ester.**

By this action diethyl-monochlor-acetoacetic ester,  $\text{CH}_2\text{Cl}-\text{COC}(\text{C}_2\text{H}_5)_2\text{CO}_2\text{C}_2\text{H}_5$ , and the corresponding dichlor derivative were formed. Diethyl-monochlor-acetoacetic ester treated with sodium methoxid gave methoxy-diethyl-acetoacetic ester,  $\text{CH}_2(\text{CH}_3\text{O})\text{COC}(\text{C}_2\text{H}_5)_2\text{CO}_2\text{C}_2\text{H}_5$ , and methoxy-methyl-ethyl acetone,  $\text{CH}_2(\text{CH}_3\text{O})\text{COCH}(\text{CH}_3)(\text{C}_2\text{H}_5)$ . Di-methoxy-diethyl-acetoacetic ester,  $\text{CH}(\text{CH}_3\text{O})_2\text{COC}(\text{C}_2\text{H}_5)_2\text{CO}_2\text{C}_2\text{H}_5$ , and di-methoxy-diethyl acetone,  $\text{CH}(\text{CH}_3\text{O})_2\text{COCH}(\text{C}_2\text{H}_5)_2$ , were also prepared.

**JAMES, J. WM., 1886.**

Ann. Chem. **231**, 245-248 ; J. Chem. Soc. **50**, 333 ; Ber. **19**, 101 (C) ; Bull. Soc. chim. **46**, 758.

**Synthesis of Acetoacetic Ester from Cyanacetone.**

The author has repeated the experiment of Matthew\* and Hodgkinson's and failed to produce any trace of acetoacetic ester from cyanacetone with hydrochloric acid or an alkali.

**SOC. FOR CHEM. INDUSTRY IN BASEL, 1886.**

D. P.† 39,564 of May 4th, 1886, Kl. 22 ; Ber. **20**, 443 (C).

**Production of Quinizins by the Action of Hydrazobenzenes on Acetoacetic Esters.**

Acetoacetic ester treated with hydrazobenzene gives phenyl-methyloxyquinizin which melts at 122°

\* See page 38.

†Original article not consulted.

· SCHIFF, ROBERT, 1886.

Ber. 19, 561.

**Some Molecular Volumes.—Acetoacetic Ester.**

B. P. = 180–180 3.  $B_0 = 754.5$  mm.  $D_4^t$  = specific gravity at  $t^\circ$   
 compared to water at  $4^\circ$   $\frac{M}{D}$  = molecular volume.

$$D_4^0 = 1.0465$$

$$D_4^8 = 1.0375$$

$$D_4^{55.8} = 0.9880$$

$$D_4^{79.2} = 0.9644$$

$$D_4^{135.5} = 0.9029$$

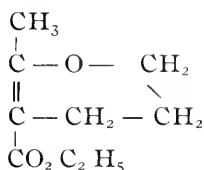
$V_t = 1. + .00109301t + .0000013895t^2 + .00000001465t^3$ , from which  
 $D_4^{180} = 0.8458$ ,  $\frac{M}{D} = 153.34$ .

**PERKIN, Jr., W. H., 1886.**

Ber. 19, 1244–1247; J. Chem. Soc. 50, 689; Jsb. Chem. 1886, 1332;  
 Bull. Soc. chim. 46, 834.

**Action of Trimethylen=bromid on Sodacetoacetic Ester.**

An oil  $C_9H_{14}O_3$ , boiling at  $223^\circ$  is obtained which cannot be an aceto-tetramethylen carboxylic ester because its properties when compared to the acetotrimethylen carboxylic ester and to the tetramethylen dicarboxylic ester are too irregular and because it will not react with phenylhydrazin. The author gives it the formula—



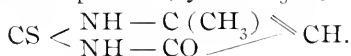
**BEHREND, ROBERT, R. LIST AND A. KOHLER, 1886.**

Ann. Chem. **233**, 1-15; Ber. **19**, 219-221; Ber. **19**, 395 (C); J. Chem. Soc. **50**, 443; Jsb. Chem. 1886, 549; Bull. Soc. chim. **46**, 544.

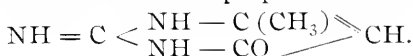
**Condensation of Carbamids with Acetoacetic Ester.**

Acetoacetic ester treated with phenylcarbamid gives a compound  $C_{13}H_{16}N_2O_3$ , which when treated with an alkali yields acetone, alcohol, carbon dioxid and analin and when treated with an acid it yields in addition to these products ethyl phenylcarbamate,  $C_9H_{11}NO_2$ .

Thiocarbamid and acetoacetic ester unite to form an unstable compound which, when saponified, yields  $C_5H_6N_2SO$  which is



Guanidin,  $CN_3H_5$ , and acetoacetic ester form a compound  $C_5H_7N_3O$ , which has both acid and basic properties. Its formula probably is

**ISBERT, A., 1886.**

Ann. Chem. **234**, 160-196; J. Chem. Soc. **50**, 1009; Ber. **19**, 684 (C); Jsb. Chem. 1886, 1328; Bull. Soc. chim. **47**, 585.

**Acetoacetic Ester and Its Derivatives.**

When acetoacetic ester is decomposed by sodium alkyl oxids in the presence of an alcohol, the acetate derived from the free alcohol is the chief product, while the acetate derived from the alkyl oxid is formed in smaller proportions. Resacetic acid,  $C_{18}H_{22}O_5$ , is formed during the same operation. Acetoacetic ester is not decomposed by ethyl or propyl alcohol at  $180^\circ$ , but is completely decomposed upon adding a little sodium alkyl oxid to such a mixture. The amid,  $C_6H_{11}NO_2$ , obtained by treating acetoacetic ester with ammonia, melts at  $90^\circ$  and is soluble in water. From its reactions the formula  $CH_3 \cdot COC_2H_5 : CH \cdot CONH_2$ , is assigned to it. Phosphoric chlorid acting on ethyl acetoacetic ester gives ethyl-mono-chloroacetoacetic acid and the ethyl esters of mono- and di-chlor-ethylacetoacetic acids, and acting on methylacetoacetic ester it forms the corresponding compounds. Ethoxy-ethyl-acetoacetic ester,  $(C_2H_5O)CH_2COC_2H_5 : CHCO_2C_2H_5$ , and ethoxy-methyl-acetoacetic ester are formed by the action of an

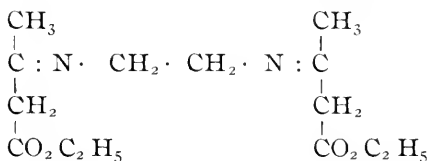
alcoholic solution of sodium ethoxid on monochlor-ethyl and monochlor methyl-acetoacetic esters and are decomposed by alcoholic soda into ethoxy-ethyl acetone,  $(C_2 H_5 O) CH_2 CO CH_2 (C_2 H_5)$ , and ethoxy-methyl acetone,  $(C_2 H_5 O) CH_2 CO CH_2 (C H_3)$ , which boil at  $112^\circ$  to  $115^\circ$  and  $100^\circ$  to  $105^\circ$  respectively.

### SOC. FOR CHEM. INDUSTRY IN BASEL, 1886.

D. P.\* 39, 149 of June 5th, 1886, Kl. 12 ; Ber. **20**, 351 (C).

#### The Production of the Ester of a New Acid.

If acetoacetic ester be treated with a water solution of ethylenediamin,  $C_2 H_4 (NH_2)_2$ , they unite to form the compound,



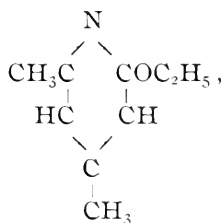
which melts at  $126^\circ$ , is insoluble in water but soluble in alcohols, ether, chloroform, benzene and dilute acids.

### CANZONERI, F. AND G. SPICA, 1886.

Gazz.\* chim. **16**, 449-453 ; Ber. **20**, 219 (C) ; J. Chem. Soc. **52**, 499.

#### Synthesis of Ethoxy-lutidin.

By treating acetoacetic ester in a sealed tube with an excess of ammoniacal zinc chlorid, ethoxy-lutidin,



\*Original article not consulted.

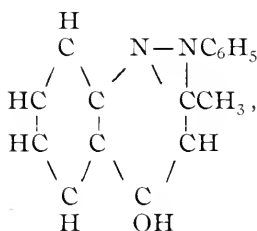
is formed, a pale yellow liquid boiling at  $245^{\circ}$  to  $247^{\circ}$ . By repeating former experiments with acetoacetic ester and formamid, a liquid boiling at  $250^{\circ}$  to  $255^{\circ}$  was obtained which was mono-lutidin-carboxylic ester and which apparently is isomeric with Michael's body of the same name which he obtained from aldehyde, aldehyde ammonia and acetoacetic ester.

### MÜLLER, ALBERT, 1886.

Ber. **19**, 1771-1772 ; J. Chem. Soc. **50**, 899 ; Jsb. Chem. 1886, 1035.

#### Action of Acetoacetic Ester on Hydrazo-benzene.

When acetoacetic ester is treated with hydrazo-benzene,  $C_6H_5NH-NHC_6H_5$ , a compound  $C_{16}H_{14}N_2O$  which melts at  $120^{\circ}$  and is weakly basic and acid is formed. It is probably a phenylated quinizin,



### ESCALES, R. AND E. BAUMANN, 1886.

Ber. **19**, 1787-1796 ; J. Chem. Soc. **50**, 878.

#### Compounds of Phenyl Mercaptan with Ketonic Acids. Phenyl Mercaptan and Acetoacetic Ester.

By treating a mixture of two molecules phenyl mercaptan and one molecule acetoacetic ester with hydrochloric acid,  $\beta$  dithiophenylbutyric ester,  $CH_3C(SC_6H_5)_2CH_2CO_2C_2H_5$ , is obtained; it melts at  $57^{\circ}$ - $58^{\circ}$ ,

is insoluble in water, soluble in ether, benzene and chloroform and gives a red color with concentrated sulfuric acid. When heated with an alkali it is decomposed into phenyl mercaptan and  $\beta$ -thio-phenylcrotonic acid,  $\text{CH}_3(\text{SC}_6\text{H}_5) : \text{CH CO}_2\text{H}$ , which melts at  $176^\circ\text{--}177^\circ$ , is insoluble in water, soluble in benzene and hot alcohol. When heated this decomposes, giving thio-phenyl-propylene,  $\text{C}_3\text{H}_5\text{SC}_6\text{H}_5$ , which boils at  $206^\circ\text{--}210^\circ$  and gives a blue color with sulfuric acid, which turns violet upon being heated.

### LIST, R., 1886.

Ann. Chem. **236**, 1-32 ; J. Chem. Soc. **52**, 127 ; Ber. **19**, 825 (C) ;  
Jsb. Chem. 1886, 564 ; Bull. Soc. chim. **47**, 587.

### Action of Thiocarbamid on Acetoacetic Ester.

Thiomethyl-uracyl is formed, thus :  $\text{CH}_3\text{COCH}_2\text{CO}_2\text{C}_2\text{H}_5 + \text{NH}_2\text{CSNH}_2 = \text{CH}_3\overset{\text{NH}-\text{C}=\text{S}-\text{NH}_2}{\underset{\text{OH}}{\text{C}}}\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$   
and then water and alcohol  
breaking off it leaves  $\text{CH}_3\overset{\text{NH}-\text{C}=\text{S}-\text{N}-\text{H}}{\underset{\text{CHC}:\text{O}}{\text{C}}}$ .

The silver, copper, mercury, potassium, and sodium salts and the methyl and ethyl esters were produced and described. The sulfur can be removed from the thiomethyl-uracyl by bromine or by silver or mercuric oxid. Thiomethyl-uracyl acetic acid,  $\text{C}_7\text{H}_8\text{N}_2\text{SO}_3$ , and its ethyl ester were made by using monochlor-acetic ester.

In the formation of the esters an intermolecular change is supposed to take place and the formulæ are written  $\text{CH}_3-\overset{\text{N}}{\underset{\text{S}-\text{R}}{\text{C}}} : \overset{\text{N}}{\underset{\text{S}-\text{R}}{\text{C}}} : \text{CH} \cdot \overset{\text{N}}{\underset{\text{S}-\text{R}}{\text{C}}} : \text{O}$

**KNORR, L., 1886.**

Ann. Chem. **236**, 69-115; J. Chem. Soc. **52**, 159; Ber. **19**, 827 (C);  
Jsb. Chem. 1886, 1336; Bull. Soc. chim. **47**, 633.

**Synthetical Experiments with Acetoacetic Ester.—Part I.**

Acetoacetic ester and anilin react at ordinary temperatures to form  $\beta$ -phenylamido- $\alpha$ -crotonic ester, but at 110°-150° the anilid of acetoacetic acid is formed, which melts at 85° and gives, when distilled, diphenyl-carbamid,  $\text{CO} < \begin{smallmatrix} \text{NHC}_6\text{H}_5 \\ \text{NHC}_6\text{H}_5 \end{smallmatrix}$ , which melts at 235°-236°. The anilid, when heated with chloroform and bromin, yields the anilid of monobrom-acetoacetic acid,  $\text{CH}_3\text{COCHBrCO NHC}_6\text{H}_5$ , which melts with decomposition at 138°. Isonitroso-acetoacetic anilid,  $\text{CH}_3\text{COC} : (\text{NOH})\text{CO NHC}_6\text{H}_5$ , is a crystalline substance melting at 99°-100°. Reducing agents change acetoacetic acid anilid into hydroxylepidin,  $\text{C}_9\text{NH}_5\text{CH}_3\text{OH}$ , [4' : 2'] which can be changed into  $\gamma$ -lepidin and chlorolepidin. Methoxy-lepidin formed from chlorolepidin boils at 275°-276°. Ethoxy-lepidin melts at 51°. Methyl-lepidone,



may be formed from methyl anilin and acetoacetic ester. It melts at 130°, sublimes and is a strong base.

**DEGEN, JOS., 1886.**

Ann. Chem. **236**, 151-164; Ber. **19**, 829 (C).

**Indol from Methyl-phenylhydrazin.**

In this article an account is given of making methyl-phenylhydrazin acetoacetic ester,  $\text{CH}_3\text{C} : (\text{N}_2\text{CH}_3\text{C}_6\text{H}_5)\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$ , from methyl-phenylhydrazin and acetoacetic ester. The product, a yellowish red oil could not be distilled, but seemed quite stable towards water solutions of the alkalis. With alcoholic potash it was decomposed into methyl-phenylhydrazin acetoacetic acid.

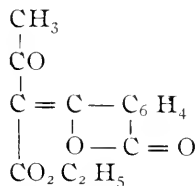


**BÜLOW, CARL, 1886.**

Ann. Chem. **236**, 184-194; J. Chem. Soc. **52**, 144; Jsb. Chem. 1886, 1515; Bull. Soc. chim. **47**, 600.

**Phthalyl=acetoacetic Ester.**

This is obtained from phthalyl chlorid and acetoacetic ester and is represented thus:



It is decomposed by sulfuric acid yielding phthalyl acetic acid. Ammonia converts it into phthalyl-diamid or phthalyl-imid according to the temperature. Several complicated derivatives were described, among them those formed by phenylhydrazin.

**KNORR, L., 1886.**

Ann Chem. **236**, 290-332; J. Chem. Soc. **52**, 275; Ber. **20**, 55 (C); Jsb. Chem. 1886, 1338; Bull. Soc. chim. **47**, 811.

**Synthetical Experiments with Acetoacetic Ester.—Part II.**

The first part of this article (pp 290-317) is devoted to diaceto succinic esters, the remainder to forming pyrrol derivatives from acetoacetic ester. This treated with sodium nitrite forms nitrosoacetoacetic ester which mixed with acetoacetic ester and reduced, gives dimethyl-pyrrol-di-carboxylic ester,  $\text{C}_4\text{NH}(\text{C}_2\text{H}_5)_2(\text{CO}_2\text{C}_2\text{H}_5)_2$  [2:4:3:5]. This melts at  $134^\circ$ - $135^\circ$  and can be distinguished from its symmetrical isomer by its absence of basic properties. By eliminating one of the ethyl groups two isomeric mono-ethyl esters of dimethyl-pyrrol-dicarboxylic acid can be produced and from these (1) by eliminating ethyl, dimethyl-pyrrol-dicarboxylic acid (2) by eliminating carbon dioxide, dimethyl-pyrrol-mono-carboxylic ester. Dimethyl-pyrrol-mono-carboxylic acid and dimethyl-pyrrol,  $\text{C}_4\text{N}(\text{CH}_3)_2\text{H}_3$ , were also produced. By using the anilid of acetoacetic ester corresponding compounds were made and their properties described.

**PERKIN, Jr., W. H. AND M. OBREMBSKY, 1886.**

Ber. **19**, 2045-2055 ; J. Chem. Soc. **50**, 936 ; Jsb. Chem. 1886, 1397.

**Upon  $\alpha_1$ - $\alpha_2$ -Diacetyl-adipic Acid.**

From the high-boiling residue from the action of ethylene bromid on sodacetoacetic ester the authors have isolated di-acetyl-adipic ester,

which is  $\begin{array}{c} \text{CH}_2 - \text{CH}(\text{CH}_3 \text{CO})\text{CO}_2 \text{C}_2 \text{H}_5 \\ | \\ \text{CH}_2 - \text{CH}(\text{CH}_3 \text{CO})\text{CO}_2 \text{C}_2 \text{H}_5 \end{array}$ . It will unite with phenyl-

hydrazin, one molecule of  $(\text{C}_6\text{H}_5\text{N}_2\text{H})''$  displacing each atom of oxygen of the carbonyl groups. Ethylene-di-methyl-oxyquinizin is also formed. The actions of diacetyl-adipic ester with alcoholic ammonia, sulfuric acid and alcoholic potash are given.

**POLONOWSKA, NATALIE, 1886.**

Ber. **19**, 2402-2406 ; J. Chem. Soc. **50**, 1011 ; Jsb. Chem. 1886, 1386.

**So-called Carbacetoacetic Ester.**

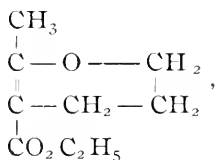
The action of hydrochloric acid on acetoacetic ester is the same as that of sulfuric producing an anhydrid,  $\text{C}_{18} \text{H}_{22} \text{O}_9$ , which breaks down into isodehydracetic acid and its ethyl ester (as shown by Hantzsch) so that Duisberg's so-called carbacetoacetic ester,  $\text{C}_8 \text{H}_{10} \text{O}_3$ , must be isodehydracetic ester,  $\text{C}_{10} \text{H}_{12} \text{O}_4$ .

**PERKIN, JR., W. H., 1886.**

Ber. **19**, 2557-2561 ; J. Chem. Soc. **52**, 32 ; Jsb. Chem. 1886, 1332.

**Action of Trimethylenbromid on Acetoacetic Ester.**

The ester,



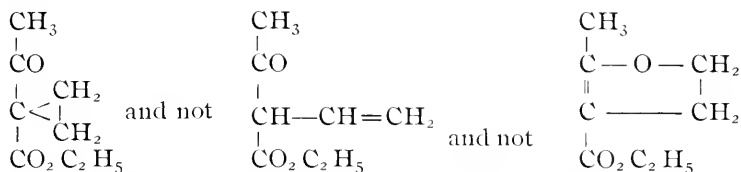
and its acid are further studied. The acid heated with water gives aceto-butyl alcohol and by distillation of this, acetobutyl alcohol anhydrid is obtained. The ester dissolves in hydrobromic acid to form brom-butyl methylketone,  $\text{CH}_3\text{CO}(\text{CH}_2)_4\text{Br}$ . Analogous compounds of some aromatic derivatives are cited.

**PERKIN, JR., W. H. AND P. C. FREER, 1886.**

Ber. **19**, 2561-2569; J. Chem. Soc. **52**, 33.

**Upon Aceto-trimethylenecarboxylic Ester.**

This substance was proven by its physical properties to have a trimethylene formula and thus to be :



It was united with hydrobromic acid to form omega-brom-ethyl-aceto-acetic ester,  $\text{CH}_3\text{COCH}(\text{CH}_2\text{CH}_2\text{Br})\text{CO}_2\text{C}_2\text{H}_5$ , which is an oil which cannot be distilled. Saponifying this oil, aceto-propyl alcohol is obtained,  $(\text{CH}_3\text{CO})\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ , and sodium amalgam reduces this to gamma-pentylene glycol,  $\text{CH}_3\text{CHOHCH}_2\text{CH}_2\text{CH}_2\text{OH}$ .

**WITT, OTTO N., 1886.**

Ber. **19**, 2977-2978 and 3299; J. Chem. Soc. **52**, 247; Jsb. Chem. 1886, 783; Bull Soc. chim. **47**, 434.

**Action of Acetoacetic Ester on Aromatic Diamins.**

Acetoacetic ester heated with ortho-toluylene-diamin  $\text{C}_6\text{H}_3\text{CH}_3(\text{NH}_2)_2$ , gives ethenyl-toluylene-diamin,  $\text{C}_6\text{H}_3\text{CH}_3 < \begin{array}{c} \text{N} \\ \text{NH} \end{array} \text{C} = \text{CH}_2$ , which melts at  $201^\circ\text{--}202^\circ$ .

In the second communication the author acknowledges the priority of Ladenburg and Rügheimer in the preparation of this compound.

**KNORR, L., 1886.**

Ann. Chem. **238**, 137-219; J. Chem. Soc. **52**, 601; Ber. **20**, 259 (C).

**Synthetical Experiments with Acetoacetic Ester.—Part III.**

The compounds obtained from the action of phenylhydrazin on acetoacetic ester, heretofore described by the author as quinizin derivatives are now considered pyrazolone derivatives, pyrazolone being

$\begin{array}{c} \text{CH}_2 - \text{CO} \\ | \\ \text{C} - \text{H} = \text{N} \end{array} > \text{NH}$ . Thus antipyrin is phenyl-dimethyl pyrazolone

[1:2:3] and not di-methyl oxyquinizin Phenylmethyl pyrazolone is described. Phenyltrimethyl pyrazolone [1:3:4:4] obtained from dimethyl-acetoacetic ester melts at 55°-56° boils at 300° to 303° and is isomeric with methyl antipyrin. Disphenyl-methyl pyrazolone, [1:3:5]

$\text{C}_6\text{H}_5\text{N} < \begin{array}{c} \text{CO} - \text{CH} - \text{CH} - \text{CO} \\ | \qquad | \\ \text{N} = \text{C} \qquad \text{C} = \text{N} \\ | \qquad | \\ \text{CH}_3 \qquad \text{CH}_3 \end{array} > \text{NC}_6\text{H}_5$ , and a number of its

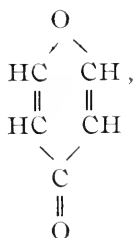
derivatives are produced and described, among which is pyrazol blue, obtained from the above by abstracting the two hydrogen atoms from the CH groups. Some of the aromatic and nitrogen compounds of the pyrazolones are described and also some halogen compounds of antipyrin.

**CONRAD, M. and M. GUTHZEIT, 1887.**

Ber. **20**, 151-154; J. Chem. Soc. **52**, 502; Jsb. Chem, 1887, 1818;  
Bull. Soc. chim. **48**, 154.

**Dimethyl-pyrondicarboxylic Ester**

This substance, obtained from cupracetoacetic ester and carbonyl chlorid, formerly called dehydro-carbonyl-diacetoacetic ester is now considered to be a derivative of pyron,



in which the methyl groups occupy the 2 and 6 places and the carboxyl groups have the 3 and 5 places. It melts at 80. Alkalis decompose it into carbon dioxid and acetoacetic ester which is further decomposed to its usual decomposition products.

JAMES, J. WM., 1887,

J. Chem. Soc. **51**, 287-290; Ann. Chem. **240**, 61-66.

#### Formation of Cyan-acetoacetic Ester.

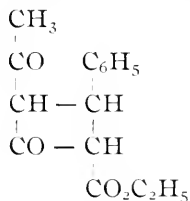
By treating monochloracetoacetic ester with potassium cyanid, potassium cyanacetoacetic ester was formed to which was given the formula  $\text{CH}_2(\text{CN})\text{COCHKCO}_2\text{C}_2\text{H}_5$ . Treating this with an acid, produced cyanacetoacetic ester, a liquid which cannot be distilled under ordinary pressure. By treating dichloracetoacetic ester, called by the author  $\text{CHCl}_2\text{COCH}_2\text{CO}_2\text{C}_2\text{H}_5$ , with potassium cyanid no corresponding compound was formed but potassium dichloracetate,  $\text{CHCl}_2\text{CO}_2\text{K}$ , was the chief product.

MICHAEL, A., 1887.

Am. Chem. J. **9**, 112-124; J. prakt. Chem. **143**, 349-357; J. Chem. Soc. **52**, 672; Ber. **20**, 258 (C) and 504 (C); Jsb. Chem. 1887, 1542; Bull. Soc. chim. **48**, 520.

#### Addition of Sodacetoacetic Ester and Sodomalonic Ester to the Esters of Unsaturated Acids.

When sodacetoacetic ester is treated with cinnamic ester they unite directly and then split off sodium ethoxid forming a compound



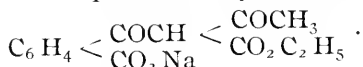
which is very unstable decomposing at 100. It acts as a mono-basic acid. Acetoacetic ester and citraconic ester,  $\text{C}_5\text{H}_4(\text{C}_2\text{H}_5)_2\text{O}_4$ , combine directly to form  $\text{C}_{15}\text{H}_{24}\text{O}_7$  an unstable oil boiling at  $173^\circ$ - $174^\circ$  at 26 m. m. pressure. The author makes the point that these substances are addition products.

**MICHAEL, A., 1887.**

J. prakt. Chem. **143**, 449-459; Am. Chem. J. **9**, 124-129; J. Chem. Soc. **52**, 716; Ber. **20**, 320 (C); Jsb. Chem. 1887, 1536; Bull. Soc. chim **48**, 521.

**Some New Reactions with Sodacetoacetic Ester.**

By the action of benzoic aldehyde on sodacetoacetic ester a compound  $C_{22}H_{20}Na_2O_7$  is formed which melts at  $126^{\circ}$ - $127^{\circ}$  and is soluble in alkalis. Mustard oils react with sodacetoacetic ester to form mono-thio-amids. Phenyl isocyanate forms two compounds with sodacetoacetic ester. Anhydrids of dibasic organic acids unite directly with sodacetoacetic ester: phthalic anhydrid forming



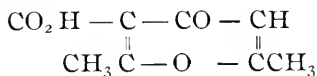
The action of phenols is to form coumarins. Ureas react to form the ureids and sulfo-ureas form the corresponding sulfo derivatives. Aldehyde ammonia forms condensation products, with sodacetoacetic ester it forms  $C_8H_{12}NaNO_2$ . Sodacetoacetic ester was also found to react with lactones, amidins, primary bases, guanidin, cyanamid, cyanic acid and benzoquinone.

**PERKIN, Jr., W. H., 1887.**

J. Chem. Soc. **51**, 484-500; Jsb. Chem. 1887, 1815.

**Dehydracetic Acid.**

After reviewing the work done by other chemists on this acid the author deduces the formula



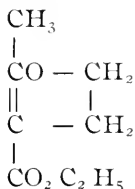
for it. The proof that it contains carbonyl is that it unites with phenylhydrazin to form  $C_8H_8O_3(N_2HC_6H_5)$ . It will form no acetyl derivative, therefore (two oxygen atoms being in the form of carboxyl) the fourth one must be between two carbon atoms. When carefully treated with potassium hydroxid, dehydracetic acid gives acetoacetic acid therefore it must contain two methyl groups. When treated with anilin, dehydracetic methyl ester forms lutidone derivatives, phenyl-lutidone-carboxylic methyl ester being first produced which is decomposed into phenyl lutidone,  $C_5NH(OH)(CH_3)_2C_6H_5$ . The bromid acetate, oxim and phenylhydrazin derivatives of dehydracetic acid were prepared and described.

FREER, P. C. AND W. H. PERKIN, Jr., 1887.

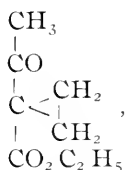
J. Chem. Soc. **51**, 820-849 ; Am. Chem. J. **10**, 446-457.

**Action of Ethylene Bromid on Sodium Derivatives of Acetoacetic Ester.....**

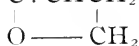
Experiments with acetoacetic ester and ethylene bromid being repeated, it was found that two substances were produced, one as before described in Ber. **19**, 2561 and the other having the formula



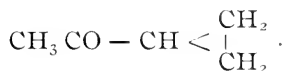
and being termed methyl-dehydropentone-carboxylic ester. The former is produced in much the larger quantities. Acetyltrimethylenecarboxylic ester,



(which is the one formerly described) when boiled with water gives acetopropyl alcohol,  $(\text{CH}_3 \text{CO}) \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{OH}$ , but upon being heated it becomes acetopropyl anhydrid,  $\text{CH}_3 \text{C} : \text{CHCH}_2$ , and acetyl-



trimethylene,



HALLER, A. AND A. HELD, 1887.

Compt. rend. **104**, 1627-1629 ; J. Chem. Soc. **52**, 799.

**Cyanacetoacetic Ester.**

This substance obtained by James (J. Chem. Soc. **51**, 287) is the same as that obtained by the authors in 1882 (Compt. rend. **95**, 235) by the action of cyanogen chlorid on sodacetoacetic ester. The authors give it the composition  $\text{CH}_3 \text{COCH} (\text{CN}) \text{CO}_2 \text{C}_2 \text{H}_5$ , not as James gave it  $\text{CH}_2 (\text{CN}) \text{COCH}_2 \text{CO}_2 \text{C}_2 \text{H}_5$ .

**WALLACH, O., 1887.**

Ann. Chem. **241**, 288-315 ; J. Chem. Soc. **54**, 37 ; Jsb. Chem. 1887, 763 ;  
Bull. Soc. chim. **50**, 297.

**Nitrosates, Nitrosites and their Derivatives.**

Amylene and nitrogen peroxid unite directly and form, not a dinitrite but a nitroso nitrate. This compound  $C_5H_{10}N_2O_4$ , unites with acetoacetic ester to form the crystalline compound  $CH_3COCH(NOC_5H_{10})CO_2C_2H_5$ .

**CLAISEN, L. AND O. LOWMAN, 1887.**

Ber. **20**, 651-654 ; J. Chem. Soc. **52**, 583 ; Jsb. Chem. 1887, 2050 ;  
Bull. Soc. chim. **48**, 394.

**Preparation of Benzolacetic Ester.**

Acetoacetic ester is formed in this operation which consists of mixing sodium ethoxid and benzoic ester and treating the product with acetic acid. The theory is advanced that here as well as in the ordinary production of acetoacetic ester an intermediate, addition product is formed. In the case of acetoacetic ester it would be  $CH_3C \begin{smallmatrix} \diagup (OC_2H_5)_2 \\ \diagdown O-Na \end{smallmatrix}$ , which is acted upon by acetic ester thus :  $-CH_3C \begin{smallmatrix} \diagup (OC_2H_5)_2 \\ \diagdown O-Na \end{smallmatrix} + H_2CHCO_2C_2H_5 = CH_3C(ONa) : CHCO_2C_2H_5 + 2C_2H_5OH$ .

**CONRAD, M. AND L. LIMPACH, 1887.**

Ber. **20**, 944-948 ; J. Chem. Soc. **52**, 679 ; Jsb. Chem. 1887, 1046 ;  
Bull. Soc. chim. **48**, 320.

**Synthesis of Quinolin Derivatives from Acetoacetic Ester.**

By heating anilacetoacetic ester,  $CH_3C(NHC_6H_5) : CHCO_2C_2H_5$ , it is decomposed and besides alcohol, acetone and carbanilid,  $CO : (NHC_6H_5)_2$ , it forms  $\gamma$ -hydroxy-quinaldin,  $C_6H_4C_3HOHCH_3N$ ,  $[OH : CH_3 = 2' : 4']$ , which melts at  $230^\circ$ - $231^\circ$  and distills at  $360^\circ$  with some decomposition. It is very bitter and gives an intensely reddish yellow color with ferric chlorid. A number of its salts and derivatives were described, phenylamidoquinaldin, methoxyquinaldin and some derivatives containing chlorin, bromin and nitrogen.



**HANTZSCH, A. AND H. ZÜRCHER, 1887.**

Ber. **20**, 1328-1332; Jsb. Chem. 1887, 1461; Bull. Soc. chim. **48**, 747.

**Polycoumarins.**

By treating polyhydric phenols with an excess of acetoacetic ester and sulfuric acid, polycoumarins are formed. Di-methyl di-coumarin,  $C_6H_2 < \left[ \begin{array}{c} CCH_3:CH \\ O \text{ --- } CO \end{array} > \right]_2$ , formed from acetoacetic ester and resorcin,  $C_6H_4(OH)_2$ , is a white powder almost insoluble in ordinary solvents, soluble in alkalis from which solution acids precipitate di-methyl dicoumaric acid,  $C_6H_2 < \left[ \begin{array}{c} CCH_3CHCO_2H \\ OH \end{array} > \right]_2$ . Acetoacetic ester treated with phloroglucin gives trimethyl tricoumarin,  $C_6 < \left[ \begin{array}{c} CCH_3CH \\ O \text{ --- } CO \end{array} > \right]_3$ , which is also a powder difficultly soluble except in alkalis from which solution the corresponding acid is obtained. These acids easily give up water and are changed back into the lactones.

**DELISLE, A., 1887.**

Ber. **20**, 2008; J. Chem. Soc. **52**, 915; Jsb. Chem. 1887, 1719;  
Bull. Soc. chim. **48**, 659.

**Action of Sulfur Dichlorid on Acetoacetic Ester.****Preliminary Notice.**

By treating acetoacetic ester with sulfur dichlorid, hydrochloric acid was given off and the mixture solidified. The new substance,  $C_{10}H_{14}O_6S$ , forms beautiful colorless crystals which are insoluble in water but soluble in barium hydroxid, forming a barium salt. The substance softens at  $75^\circ$  and melts at  $90^\circ$  to  $91^\circ$ .

**BENDER, G., 1887.**

Ber. **20**, 2747-2752; J. Chem. Soc. **54**, 53.

**Action of Phenylhydrazin on Chloracetoacetic Ester.**

By this action a compound  $C_{12}H_{14}N_2O_2$  was formed, it is probable that  $CH_3C(N_2HC_6H_5)CHClCO_2R$  is first formed which changes first into  $CH_3CH(N_2C_6H_5)CHClCO_2R$  and then into  $CH_3C(N_2C_6H_5):CHCO_2R$  which is  $\beta$ -phenylazocrotonic ester, melting at  $50.5^\circ$ . This can be reduced to phenylmethyl-pyrazolone.

$\alpha$ -Naphthylamin and chloracetoacetic ester unite to form a compound  $C_{16}H_{16}NO_2Cl$ , which melts at  $75^\circ$ .

**JAPP, FRANCIS AND FELIX KLINGEMANN, 1887**Ber. **20**, 2942-2944.**Benzene-azo= and Benzenehydrazo-fatty Acids.**

When sodium-methyl-acetoacetic ester is treated with diazobenzene-chlorid,  $C_6H_5N_2Cl$ , the diazo group takes the place of the acetyl group and benzene- $\alpha$ -azo-propionic ester,  $C_6H_5N_2CH(CH_3)CO_2C_2H_5$ , is produced. It is a yellow crystalline substance which melts at  $117^\circ$ . The free acid and a number of its aromatic derivatives were produced from it.

**SCHIFF, HUGO, 1887.**Ann. Chem. **244**, 19-28; J. Chem. Soc. **54**, 572.**Compounds of Sugars with Aldehydes and Acetone.**

Among other compounds described in this article is the one obtained from sugar and acetoacetic ester, corresponding to the formula  $C_6H_{10}O_3C_6H_{12}O_6$ , which is quite stable.

**CONRAD, M. AND W. EPSTEIN, 1887.**Ber. **20**, 3052-3058; J. Chem. Soc. **54**, 253; Jsb. Chem. 1887, 1719; Bull. Soc. chim. **49**, 639.**Action of Ammonia on Acetoacetic Esters.**

Amido-acetoacetic methyl ester,  $CH_3C \cdot (NH_2) : CHCO_2CH_3$ , prepared from acetoacetic methyl ester and ammonia gas is a colorless crystalline substance, which melts at  $85^\circ$  and sublimes unchanged. Amido-ethylacetoacetic methylester,  $CH_3C \cdot (NH_2) C(C_2H_5)CO_2CH_3$ , formed from ethylacetoacetic methyl ester, melts at  $36^\circ-37^\circ$ . Referring to Brandes' obtaining two compounds from this reaction the author thinks it probable that he had some acetoacetic ester with his ethyl-acetoacetic ester and so obtained the two corresponding compounds, Amido-acetoacetic esters acted upon by sodium form sodium compounds which with an alkyl iodid form amidoalkylacetoacetic esters. Amido-ethyl-acetoacetic ethyl ester formed similarly melts at  $60^\circ$ . Di-ethyl-acetoacetic ester will give no amid which proves that these compounds

are amido-crotonic-esters and not imido-butyric esters. An interesting fact is noted in regard to the melting points of these compounds. Introducing a methyl into the *methyl* ester lowers the melting point  $26^{\circ}$  and introducing an ethyl lowers it  $8^{\circ}$ , while in the *ethyl* ester the introduction of a methyl raises the melting point  $15^{\circ}$  and the introduction of an ethyl raises it  $23^{\circ}$ .

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**JAPP, FRANCIS AND FELIX KLINGEMANN, 1887.**

Ber. **20**, 3284-3286 and 3398-3401.

**Benzene-azo- and Benzenehydrazopropionic Acids.**

Discussion is taken up in regard to the constitution of the benzene- $\alpha$ -azopropionic acid, before described, and the formula is changed to  $\text{CH}_3\text{C}(:\text{NH}=\text{N}-\text{C}_6\text{H}_5)\text{CO}_2\text{H}$ , as it is found to be identical with phenylhydrazin pyrroacemic acid.

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**PETERS, T., 1887.**

Ber. **20**, 3318-3324; J. Chem. Soc. **54**, 253; Jsb. Chem. 1887, 3318; Bull. Soc. chim. **49**, 696.

**Action of Aqueous Ammonia on Alkylated Acetoacetic Esters and of Alcohols on the Carboxylic Alkyl Group in Acetoacetic Esters.**

Repeating Brandes' experiment with aqueous ammonia, the author obtained with ethyl-acetoacetic ester besides amido-ethyl-acetoacetic ester, an ethyl-acetoacetamid,  $\text{CH}_3\text{COCH}(\text{C}_2\text{H}_5)\text{CONH}_2$  melting at  $96^{\circ}$  which is undoubtedly Brandes' second body. Methyl-, isobutyl- and isoamyl-acetoacetamids were obtained from the corresponding esters; they melt respectively at  $73^{\circ}$ ,  $85^{\circ}$  and  $127^{\circ}$ . The author finds that the isobutyl and isoamyl esters may be readily prepared by the action of the respective alcohol on the ethyl ester, especially in the presence of a small quantity of sodium.

**OTTO, ROBERT, 1888.**Ber. **21**, 89-99; J. Chem. Soc. **54**, 360.**Analogy between the Ketonic Acids and the Alkyl Sulfones of the Fatty Acids.**

Some alkyl sulfones of the fatty acids of the formulæ  $\text{RSO}_2\text{CO}_2\text{H}$ ;  $\text{RSO}_2\text{CH}_2\text{CO}_2\text{H}$  and  $\text{RSO}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$  were described and the points of resemblance between them and the corresponding ketonic acids pointed out.

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**BERGREEN, HENRY, 1888.**Ber. **21**, 337-352; J. Chem. Soc. **54**, 444; Bull. Soc. chim. **50**, 556.**Thiocarbonyl Chlorid.**

The action of thiocarbonyl chlorid on sodium and copper acetoacetic esters is given in this article (Ber. pps. 347-348) by which is produced thiocarbonylacetoacetic ester, a solid which softens at  $152^\circ$  and melts at  $156^\circ$  to  $162^\circ$ . The formula  $[\text{CH}_3\text{COC}(\text{CS})\text{CO}_2\text{C}_2\text{H}_5]_x$  is ascribed to it, as the author thinks it is not a simple molecule. It will not react with phenylhydrazin or hydroxyl-amin. Thiocarbonyl chlorid acting on sodium methyl-acetoacetic ester produces an oil free from chlorin, which contains sulfur. It cannot be distilled and no crystalline product can be obtained from it.

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**BONGARTZ, J., 1888.**Ber. **21**, 478-487; J. Chem. Soc. **54**, 478.**Compounds of Aldehydes, Ketones and Ketonic Acids with Thioglycollic Acid.**

The action of hydrochloric acid gas on a mixture of thioglycollic acid and acetoacetic ester is given in this article (Ber. p. 485) by which a white crystalline powder is formed which melts at  $95^\circ$  to  $96^\circ$ . It is acetoacetic ester dithioglycollic acid and has the formula



**HALLER, A. AND A. HELD, 1888.**

Compt. rend. **105**, 115-117 ; J. Chem. Soc. **52**, 1029.

**Cyan-acetoacetic Ester.**

A new method of producing this compound is given. Cyanacetic ester dissolved in alcohol is mixed with sodium dissolved in alcohol and acetyl chlorid in ether. The equation given is  $2 \text{CH}(\text{CN})\text{NaCO}_2\text{C}_2\text{H}_5 + \text{CH}_3\text{COCl} = \text{NaCl} + \text{CH}_2(\text{CN})\text{CO}_2\text{C}_2\text{H}_5 + \text{CH}_3\text{COC}(\text{CN})\text{NaCO}_2\text{C}_2\text{H}_5$ . This shows conclusively that the composition of the compound is that here assigned to it.

**HALLER, A. AND A. HELD, 1888.**

Compt. rend. **106**, 210-213 ; Bull. Soc. chim. **49**, 243 ; J. Chem. Soc. **54**, 579 ; Ber- **21**, 187 (C).

**Cyan-acetoacetic Methyl Ester.**

This body,  $\text{CH}_3\text{COCH}(\text{CN})\text{CO}_2\text{CH}_3$ , was prepared from cyanogen chlorid and a mixture of acetoacetic methyl ester and sodium methoxid. It melts at  $46.5^\circ$ . It was also prepared by treating sodcyanacetic methyl ester with acetyl chlorid. The sodium and calcium compounds were prepared.

**GENVRESSE, P., 1888.**

Compt. rend. **107**, 687-689 ; J. Chem. Soc. **56**, 122 ; Ber. **21**, 831 (C).

**Chlorin Derivatives of Acetoacetic Ester.**

Dichlor-acetoacetic ester can be decomposed by hydrochloric acid into unsymmetrical dichloracetone, wherefore, (?) the formula  $\text{CHCl}_2\text{COCH}_2\text{CO}_2\text{C}_2\text{H}_5$  is assigned to it. For similar reasons the trichlor-derivative is supposed to be  $\text{CCl}_3\text{COCH}_2\text{CO}_2\text{C}_2\text{H}_5$ , tetrachlor derivative  $\text{CCl}_3\text{COCHClCO}_2\text{C}_2\text{H}_5$ , and the penta-chlor derivative  $\text{CCl}_3\text{COCCl}_2\text{CO}_2\text{C}_2\text{H}_5$ . Two compounds containing, one, seven and the other nine atoms of chlorin were also produced, described and given the formulæ  $\text{CCl}_3\text{COCCl}_2\text{CO}_2\text{C}_2\text{H}_3\text{Cl}_2$  and  $\text{CCl}_3\text{COCCl}_2\text{CO}_2\text{CHCl}_4$ . Acetoacetic methyl ester yields similar derivatives.

**GEUTHER, A., 1888.**

Ann. Chem. **244**, 190-221; J. Chem. Soc. **54**, 579; Ber. **21**, 295 (C).

**Constitution of Acetoacetic, Succinosuccinic and  
Quinone=hydro-dicarboxylic Acids.**

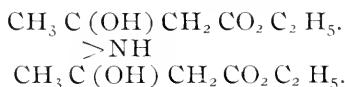
The author contends for the constitution of acetoacetic ester as  $\text{CH}_3\text{COH} : \text{CHCO}_2\text{C}_2\text{H}_5$ , giving as a proof of the hydroxyl group the similarity of reactions between acetoacetic ester and phenol and salicylic ester, (1) towards potassium hydroxid and then carbon dioxid when, he states, the original substances are regained, (2) towards potassium cyanid, when potassium compounds are produced, although the potassium compounds of salicylic and succinosuccinic esters are decomposed into alcohol and the potassium salts and the acetoacetic ester compound is decomposed into alcohol and the potassium salt, which latter is then further decomposed into potassium carbonate and acetone. (3) towards ferric chlorid, as to the colors produced. He cites the easy decomposition of acetyl-acetoacetic ester as a proof that it has the formula  $\text{CH}_3\text{CO}(\text{COCH}_3) : \text{CHCO}_2\text{C}_2\text{H}_5$ . In the formation of sod-acetoacetic ester he supposes the intermediate bivalent group  $\text{CH}_3\text{CONa} :$  is formed which unites with acetic ester liberating two atoms of hydrogen.

**MEISTER, JOHANNES, 1888.**

Ann. Chem. **244**, 233-253; J. Chem. Soc. **54**, 675; Ber. **21**, 427 (C).

**Condensation Product of Urethane and Acetoacetic Ester.**

Acetoacetic ester and urethane condense thus:  $\text{CH}_3\text{COCH}_2\text{CO}_2\text{R} + \text{NH}_2\text{CO}_2\text{C}_2\text{H}_5 = \text{CH}_3\text{C} \begin{array}{l} \nearrow \text{NHCO}_2\text{C}_2\text{H}_5 \\ = \text{CHCO}_2\text{C}_2\text{H}_5 \end{array} + \text{H}_2\text{O}$ . The product is the same as that produced from chlor-carbonic ester and paramido-acetoacetic ester and so is given the above formula. Alcoholic potash saponifies it giving an oil  $\text{C}_{12}\text{H}_{23}\text{NO}_6$ , considered as



A tribrom-derivative of the condensation product was formed but a trichlor-derivative could not be formed.

Alcoholic ammonia acts on it to form a body  $C_7H_{15}N_3O_3$ , which may be represented thus:— $CH_3C \begin{array}{l} \nearrow NHCONH_2 \\ \searrow CHC-OH \\ \quad \quad \quad \searrow OC_2H_5 \end{array}$  and which is

$\beta$ -uramidocrotonic amid together with one molecule of alcohol. Boiling this with water decomposes it into urea, acetone, alcohol, carbon dioxid and ammonia.

### MEWES, W., 1888.

Ann. Chem. **245**, 58-84; J. Chem. Soc. **54**, 817; Ber. **21**, 473 (C).

#### Halogen Substitution Products of Acetoacetic Ester and their Behavior with Sodethoxid.

Passing chlorin through acetoacetic ester produces the mono-, di-, tri- and tetra-chlor-acetoacetic esters which boil at  $194^\circ$ ,  $205^\circ$ - $207^\circ$ ,  $223^\circ$ - $225^\circ$ , and  $245^\circ$ - $250^\circ$  respectively. Some difficulty was found in entirely separating them from one another. The bromo-chlor-acetoacetic esters were formed by treating the chlor-acetoacetic esters with bromin and also by treating the bromo-acetoacetic esters with chlorin. Sodethoxid decomposes all of the halogen derivatives forming the mono- or di-halogen acetic esters. Bromoacetoacetic ester with sodethoxid yields succinosuccinic ester. When the chlorobrom-substitution products are treated with sodethoxid, sodium *bromid* is always formed.

### KNORR, L., 1888.

Ann. Chem. **245**, 357-382; J. Chem. Soc. **54**, 1111; Ber. **21**, 628 (C).

#### Synthetical Researches on Acetoacetic Ester. Part IV.

Methyl-acetoacetic anilid,  $CH_3COCH(CH_3)CONHC_6H_5$ , which was prepared from methyl-acetoacetic ester and anilin, melts at  $138^\circ$  to  $140^\circ$ . Sulfuric acid changes it into dimethyl-carbostyryl [ $3':4'$ ], a weak acid from which the dimethyl product  $C_9H_4OH(CH_3)_2N$  was obtained. Chlor-dimethyl-quinolin [ $Cl:(CH_3)_2=2':3':4'$ ], ortho- [ $4':1$ ], meta- and para- [ $4':3$ ] dimethyl-quinolin were described together with some phenyl, nitrogenous derivatives.

**JAPP, FRANCIS AND FELIX KLINGMANN, 1888.**Ber. **21**, 549-551.**Formation of Mono- and Di-hydrazin Derivatives of  $\alpha$ -Di-ketones.**

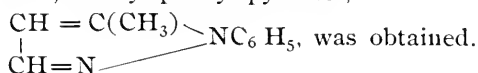
Methyl-acetoacetic acid and diazobenzene chlorid,  $C_6H_5N_2Cl$ , react and form the monophenylhydrazin derivative of diacetyl,



which melts at  $133^\circ$ . If treated with phenylhydrazin the di-phenylhydrazin derivative is formed. Ethyl-acetoacetic acid reacts similarly and gives rise to the corresponding compounds.

**CLAISEN, L. AND N. STYLOS, 1888.**Ber. **21**, 1144-1149; J. Chem. Soc. **54**, 671.**Acetoacetic-aldehyde.**

The sodium compound of acetoacetic-aldehyde,  $CH_3COCHNaCHO$ , was prepared from acetone, formic ester and sodium ethoxid. The free aldehyde could not be isolated on account of its tendency to break down into symmetrical triacetyl benzene, which was made and described. The anilid, toluidid and naphthalid of the aldehyde were prepared. Treated with phenylhydrazin, methyl-phenyl-pyrazole,

**PECHMANN, H. v., 1888.**Ber. **21**, 1411-1422; J. Chem. Soc. **54**, 811. **$\alpha$ -Diketones.**

The diketones described in this article are prepared from monoalkyl acetoacetic esters, by saponifying with dilute alkali, treating the product with sodium nitrite and sulfuric acid and after removing the alcohol by distillation, adding twenty times the volume of dilute sulfuric acid and distilling with steam. Methyl-acetoacetic ester treated in this manner gives diacetyl,  $CH_3COCOCH_3$ , and ethyl-acetoacetic ester gives acetyl-propionyl,  $CH_3COCOCH_2CH_3$ .



**BEYER, C. AND L. CLAISEN, 1888.**Ber. **21**, 1697-1705.**Mixed Azo Compounds.**

In this article some azo compounds are described which are formed from acetoacetic esters.

**GRIESS, P. AND G. HARROW, 1888.**Ber. **21**, 2740-2743; J. Chem. Soc. **54**, 1313.**Action of Acetoacetic Ester on Hexamethylenetetramin.**

When acetoacetic ester acts on hexamethylenetetramin,  $(\text{CH}_2)_6\text{N}_4$ , in presence of zinc chlorid, lutidin-di-carboxylic ester and hydro-lutidin-di-carboxylic ester are formed. The latter,  $\text{C}_5\text{NHH}_2(\text{CH}_3)_2(\text{CO}_2\text{C}_2\text{H}_5)_2$ , melts at  $170^\circ$ , is neutral and is considerably decomposed upon being distilled. Treated with hydrochloric acid it gives two products, the mono- and di-ethyl esters of lutidin-dicarboxylic acid.

**MICHAEL, A., 1888.**

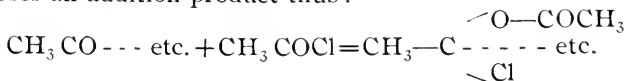
J. prakt. Chem. **145**, 473-530; Am. Chem. J. **10**, 158-160; J. Chem. Soc. **54**, 1054; Ber. **21**, 530 (C); Bull. Soc. chim. **50**, 690.

**Constitution of Sodacetoacetic Ester.**

By the action of chlor-carbonic ester on sodacetoacetic ester, carb-ethoxacetoacetic ester was produced which boils unchanged at  $127^\circ$  at 17 m.m. pressure. No sodium derivative of this could be prepared, consequently it was considered to be an isomer of aceto-malonic ester, which does easily form a sodium derivative, and its formation was supposed to be thus:— $\text{CH}_3\text{CONa}:\text{CHCO}_2\text{C}_2\text{H}_5 + \text{ClCO}_2\text{C}_2\text{H}_5 = \text{CH}_3\text{CO}(\text{CO}_2\text{C}_2\text{H}_5):\text{CHCO}_2\text{C}_2\text{H}_5 + \text{NaCl}$ . In the author's opinion acetoacetic ester itself is a ketone. He gives as a formula for benzalacetoacetic ester  $\text{CH}_3\text{C}:\text{C}:\text{CO}_2\text{C}_2\text{H}_5$ , which explains its loss of ketone properties



and to explain the reactions between bodies analogous to acetoacetic ester such as levulinic acid,  $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CO}_2\text{H}$ , and acetyl chlorid, he supposes an addition product thus:—



and a subsequent separation of hydrochloric acid forming a lactone.

In the formation of sodacetoacetic ester an aldol polymerization is supposed to take place first, the product of which is acted upon by

sodium thus : —  $2 \text{CH}_3 \text{CO}_2 \text{C}_2 \text{H}_5 = \text{CH}_3 \text{C} \begin{array}{l} \nearrow \text{OC}_2 \text{H}_5 \\ \searrow \text{OH} \end{array} \text{CH}_2 \text{CO}_2 \text{C}_2 \text{H}_5$ , then

sodium forms  $\text{CH}_3 \text{C} \begin{array}{l} \nearrow \text{OC}_2 \text{H}_5 \\ \searrow \text{ONa} \end{array} \text{CH}_2 \text{CO}_2 \text{C}_2 \text{H}_5$ , which is again acted upon by

sodium to form  $\text{CH}_3 \text{CONaCHCO}_2 \text{C}_2 \text{H}_5$ ,  $\text{NaOC}_2 \text{H}_5$  and  $\text{H}$ . If sodium be made to act on acetoacetic ester,  $\text{CH}_3 \text{COCHNaCO}_2 \text{C}_2 \text{H}_5$  is formed but the sodium is immediately attracted to the carbonyl group and it changes to form  $\text{CH}_3 \text{CONa:CHCO}_2 \text{C}_2 \text{H}_5$ . When this last compound is treated with an alkyl iodid,  $\text{C}_2 \text{H}_5 \text{I}$  for example, there is an addition product formed and as the group  $\text{—CONa=}$  is more positive than the group  $\text{=CH—}$ , the iodine adds to the former and the ethyl adds to the

$\text{=CH—}$  group forming  $\text{CH}_3 \text{C} \begin{array}{l} \nearrow \text{ONa} \\ \searrow \text{I} \end{array} \text{CH}(\text{C}_2 \text{H}_5) \text{CO}_2 \text{C}_2 \text{H}_5$  from which

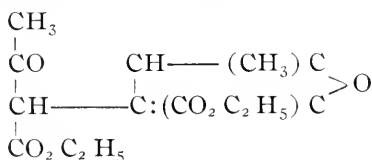
sodium iodide separates leaving  $\text{CH}_3 \text{COCH}(\text{C}_2 \text{H}_5) \text{CO}_2 \text{C}_2 \text{H}_5$ .

### POLONOWSKY, M., 1888.

Ann. Chem. **246**, 1-32 ; J. Chem. Soc. **54**, 1067 ; Ber. **21**, 636 (C).

#### Condensation of Glyoxal with Acetoacetic Esters.

By treating a mixture of glyoxal,  $\text{CHOCHO}$ , and acetoacetic ester with zinc chloride two products are formed, (1) a part soluble in alkalis which contains methyl-furfuran carboxyacetic or sylvanecarboxyacetic acid,  $\text{O} < \begin{array}{l} \text{C}(\text{CH}_2 \text{CO}_2 \text{H}) : \text{CH} \\ \text{C}(\text{CH}_3) : \text{C}(\text{CO}_2 \text{H}) \end{array} >$ , which melts at  $207^\circ$ . The normal and acid, methyl and ethyl esters were produced and described ; (2) a part insoluble in alkalis which consists of a heavy oil and a crystalline substance, both having the composition  $\text{C}_{14} \text{H}_{18} \text{O}_6$ . The oil is di-ethyl-sylvane-carboxy-acetoacetic ester which is :—



**JAECKLE, A., 1888.**

Ann. Chem. **246**, 32-52 ; J. Chem. Soc. **54**, 1103 ; Ber. **21**, 638 (C).

**Higher Homologues of the Synthetical Pyridins and Piperidins.**

The normal propyl-lutidin hydrodicarboxylic ester,  $C_5NH_2(CH_3)_2C_3H_7(CO_2C_2H_5)_2$ , obtained from normal butaldehyde and ammonia acting on acetoacetic ester and alcohol, is a crystalline substance melting at  $118^\circ$ . From this the normal propyl-lutidin-dicarboxylic ester, the free acid and the normal propyl-lutidin were prepared. Hexyl-lutidin hydrodicarboxylic ester was prepared from ammonia, acetoacetic ester and oenanthol,  $C_6H_{13}CHO$ , and from it normal hexyl-lutidin,  $C_5NH_2(CH_3)_2C_6H_{13}$ . A number of piperidins were obtained from the corresponding pyridins and described.

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**WISLICENUS, WILHELM, 1888.**

Ann. Chem. **246**, 306-309.

**Synthesis of Ketone Acid Esters.**

As a portion of this article the author briefly reviews the controversy as to the formation of acetoacetic ester from sodium and acetic ester. He thinks that sodium acts on alcohol to form sodethoxid and liberate hydrogen, that the sodethoxid reacts with acetic ester to produce sodacetoacetic ester and alcohol and that thus alcohol is continually produced and used up again. Some of the hydrogen is used up in secondary reactions and some is given off. He doubts the formation of a sodacetic ester as an intermediate product.

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**JAPP, FRANCIS R. AND FELIX KLINGEMANN, 1888.**

Ann. Chem. **247**, 190-225 ; J. Chem. Soc. **53**, 519-544.

**Constitution of the So-called Mixed Azo Compounds.**

The compounds treated of in this article were prepared from acetoacetic esters.

**PECHMANN, H. v., 1888.**Ber. **21**, 3005-3006 ; J. Chem. Soc. **56**, 42.**Condensation Product of Quinone and Acetoacetic Ester,**

When quinone,  $C_6H_4O_2$ , is brought in contact with acetoacetic ester in the presence of zinc chlorid they react to form a substance  $C_{16}H_{16}O_6$ , which melts at  $184^\circ$ . This substance will not react with phenylhydrazin, benzoic chlorid, sodium ethoxid or alkyl iodids. Treated with potassium hydroxid and then an acid a crystalline dibasic acid  $C_{14}H_{12}O_6$  is formed which is insoluble in ordinary solvents and sublimes without melting. The salt  $C_{14}H_{10}K_2O_6 + 2H_2O$  was prepared.

**CLAISEN, L. AND W. ZEDEL, 1888.**Ber. **21**, 3397-3398 ; J. Chem. Soc. **54**, 377.**Action of Chlorcarbonic Ester on the Sodium Derivatives of Acetylacetone, Acetoacetic Ester and Malonic Ester.**

The product obtained by treating acetoacetic ester with chlorcarbonic ester was thought to be the dicarboxylic ester of acetoacetic ester and to have the formula  $CH_3COC(CO_2C_2H_5)_2CO_2C_2H_5$ .\*

**CLAISEN, L., 1888.**Ber. **21**, 3567.**A Correction.**

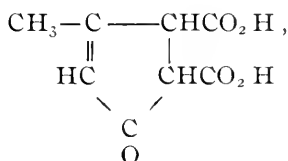
By further experiments the author has decided that the compound formed from acetoacetic ester and chlorcarbonic ester is the mono- not the di-carboxylic derivative of acetoacetic ester, that it is  $CH_3COCH(CO_2C_2H_5)CO_2C_2H_5$  and not  $CH_3COC(CO_2C_2H_5)_2CO_2C_2H_5$  as stated by him in Ber. **21**, 3397.†

\*See following article.

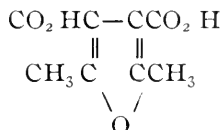
†See preceding article.

**KNORR, L., 1889.**Ber. **22**, 146-152 ; J. Chem. Soc. **56**, 384.**Constitution of Carbopyrotritartaric Acid.**

Fittig gives this acid the unsymmetrical formula



while the author gives it a symmetrical one :—



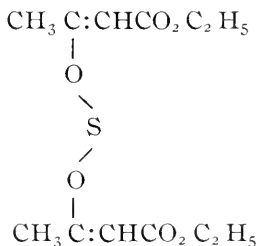
and says that this formula is proven by the fact that only one pyrotritartaric acid and only one hydrogen-ethyl ester can be formed from it.

**RAYMANN, B. AND K. CHODOUNSKY, 1889.**Ber. **22**, 304-305 ; J. Chem. Soc. **56**, 485.**Rhamnodiazin.**

Rhamnodiazin,  $\text{C}_{18}\text{H}_{32}\text{N}_2\text{O}_8$ , is formed from rhamnose,  $\text{CH}_3(\text{CHOH})_4\text{CHO}$ , and ammonia and acetoacetic ester in methyl alcohol solution. It melts at  $186^\circ$ . Other glucoses seem to yield similar compounds when treated with acetoacetic ester and ammonia.

**DELISLE, A., 1889.**Ber. **22**, 306-309 ; J. Chem. Soc. **56**, 488.**Ketosulfids and Ketosulfid Acids.**

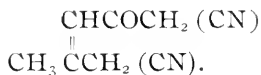
The compound described in Ber. **20**, 2008, obtained from acetoacetic ester and sulfur dichlorid is found to be  $C_{12}H_{18}O_6S$  instead of  $C_{10}H_{14}O_6S$  and the formula



is ascribed to it.

**HELD, A., 1889.**Ann. chim. phys. [6] **18**, 468-531 ; Ber. **23**, 287 (C).**Derivatives of Cyanacetoacetic Esters.**

The first part of this article is the same as that in Bull. Soc. chim. [3]<sup>1</sup>, 306\*. By treating cyanacetoacetic ester with ammonia, amidocyanacetoacetic ester,  $CH_3 C(NH_2):C(CN)CO_2 R$ , is obtained which melts at  $188^\circ$ . It is neutral wherefore the above formula is given to it. When it is treated with an alkali, sodcyanacetoacetic ester is obtained. If sulfuric acid be added to the mother liquor left after the formation of the above, a monobasic acid  $C_7 H_6 N_2 O_2$  is obtained. The sodium, barium, ammonium, silver, copper and lead salts and ethyl ester were described. When heated with hydrochloric acid, carbon dioxide is given off and another acid  $C_6 H_7 NO_2$  is formed. The author is at work on the constitution of these acids. Ethylamin acts on cyanacetoacetic ester to produce the compound  $CH_3 C(NHC_2 H_5):C(CN)CO_2 R$  and the acid  $C_9 H_{10} N_2 O_3$ . Cyanacetoacetic ester boiled with water gives  $C_8 H_8 N_2 O$  which sublimates at  $200^\circ$  and is a condensation product of cyanacetone,



\*See page 105.

**HALLER, A. AND A. HELD, 1889.**

Compt. rend. **108**, 516-518; J. Chem. Soc. **56**, 588; Ber. **22**, 255 (C).

**Monochlor-acetoacetic Esters.**

Two monochlor derivatives of acetoacetic ester were formed, the  $\alpha$ , and the  $\gamma$ . The latter by passing chlorin into acetoacetic ester at low temperatures. It boils at  $188^{\circ}$ - $189^{\circ}$ . It can be distinguished from the  $\alpha$  product by the fact that the latter readily forms an insoluble cyanid with potassium cyanid.

**HELD, A., 1889.**

Bull. Soc. chim. [3] **1**, 306-311; Ber. **22**, 407 (C); J. Chem. Soc. **56**, 1141.

**Derivatives of Cyanacetoacetic Ester.**

Bromin reacts with cyanacetoacetic ester to form a dibrom derivative,  $\text{CH}_2 \text{BrCOCBr} (\text{CN}) \text{CO}_2 \text{C}_2 \text{H}_5$ , a yellowish red liquid which decomposes upon being distilled even under reduced pressure. Chlorin forms with cyanacetoacetic ester  $\text{C}_6 \text{H}_7 (\text{CN}) \text{Cl}_2 \text{O}_3$ , which boils at  $90^{\circ}$  to  $105^{\circ}$  with 20 to 25 m. m. pressure and decomposes spontaneously. Ethyl-cyanacetoacetic ester  $\text{CH}_3 \text{COC} (\text{C}_2 \text{H}_5) (\text{CN}) \text{CO}_2 \text{C}_2 \text{H}_5$ , prepared from ethyl-sodacetoacetic ester and cyanogen chlorid, boils at  $103^{\circ}$  to  $105^{\circ}$  at 25 m. m. pressure. Potassium hydroxid decomposes it into acetic and butyric acids. Methyl-cyanacetoacetic ester prepared similarly boils at  $90^{\circ}$  to  $92^{\circ}$  at 20 m. m. pressure. Potassium hydroxid decomposes it into acetic and propionic acids. Unsuccessful attempts were made to prepare cyanacetoacetic acid.

**CURTIUS, TH. AND R. JAY, 1889.**

J. prakt. Chem. [2] **39**, 27-58; Ber. **22**, 134 (C); J. Chem. Soc. **56**, 393.

**Hydrazin.**

On pages 51 and 52 of this article the reaction between acetoacetic ester and hydrazin hydrate,  $\text{N}_2 \text{H}_4 \cdot \text{H}_2 \text{O}$ , is treated of. Methyl pyrazolone,

$$\begin{array}{c} \text{H}_2\text{C}-\text{CO} \\ | \\ \text{CH}_3\text{C}=\text{N} \end{array} > \text{NH},$$
 is formed which is a crystalline substance

melting at  $215^{\circ}$ , which will dissolve in both acids and alkalis.

**BIGINELLI, P., 1889.**

Gazz.\* chim. **19**, 212-214 ; Ber. **22**, 688 (C) ; J. Chem. Soc. **58**, 768.

**Action of Acetoacetic Ester on Cinnamaldehyde.**

When acetoacetic ester, cinnamaldehyde and ethylen-diamin are mixed and heated, a reaction takes place and a crystalline substance,  $C_{21}H_{26}O_6$  is formed which melts at  $160^{\circ}$ - $161^{\circ}$ . It will give a bromin derivative and is decomposed by caustic potash. Methylamin or anilin may be used in place of ethylendiamin without changing the result. If benzaldehyde be used in place of cinnamaldehyde a compound free from nitrogen is obtained but if propaldehyde is used a compound containing nitrogen is produced.

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**BIGINELLI, P., 1889.**

Gazz.\* chim. **19**, 215-217 ; Ber. **22**, 689 (C) ; J. Chem. Soc. **58**, 732.

**Action of Acetoacetic Ester on Dextrose in  
Alcoholic Ammonia.**

In this reaction two compounds are formed,  $C_{16}H_{26}O_8N$  a neutral substance which melts at  $189^{\circ}$ - $190^{\circ}$  and  $C_{10}H_{16}O_5N$ , which melts at  $130^{\circ}$ - $131^{\circ}$ . The latter was formed in sealed tubes at  $100^{\circ}$  to  $110^{\circ}$ . The author is continuing the investigation of these reactions.

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**KIPPING, F. STANLEY AND W. H. PERKIN, Jr., 1889.**

J. Chem. Soc. **55**, 330-351 ; Ber. **22**, 571 (C).

 **$\alpha$ - $\omega$ -diacetyl-pentane and  $\alpha$ - $\omega$ -dibenzoyl-pentane.**

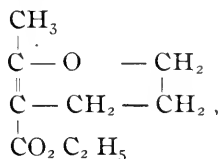
In the researches upon these compounds the first one was made from acetoacetic ester. Sodacetoacetic ester was treated with trimethylene bromid and after the reaction more sodium dissolved in alcohol was

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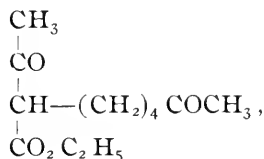
\*Original article not consulted.



added. This process gave a much better yield than any other method tried. The product obtained is methyl-dehydrohexone carboxylic ester,



This is changed by hydrobromic acid into aceto-butyl-bromid,  $\text{CH}_3 \text{CO} (\text{CH}_2)_4 \text{Br}$ , and this by sodacetoacetic ester into  $\alpha$ - $\omega$ -diacetylcaproate.



Treating this with potassium hydroxid the free acid is produced and by heating this carbon dioxid is given off and  $\alpha$ - $\omega$ -diacetyl-pentane,  $\text{CH}_3 \text{CO} (\text{CH}_2)_5 \text{COCH}_3$ , is obtained. Several derivatives of this are described.

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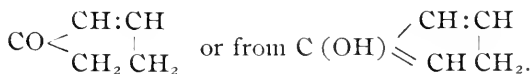
FITTING, R., FRITZ VON EYERN AND ADOLF DIETZEL, 1889,

Ann. Chem. **250**, 166-211; J. Chem. Soc. **56**, 592;

Ber. **22**, 200 (C).

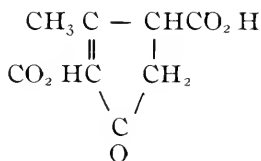
### Condensation of $\beta$ -Ketonic Esters with Dibasic Acids.

After a discussion of the constitution of the products of condensation of succinic and pyruvic acids with acetoacetic ester, it is decided that they are all derived from, either

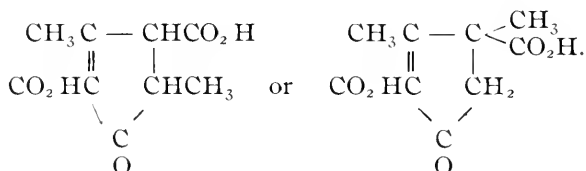


Pyrotritartaric acid is now called uvitic acid and carbpyrotritartaric acid is now called carbuvtic acid. When acetoacetic ester, acetic anhydrid and sodium succinate are heated together they give hydrogen

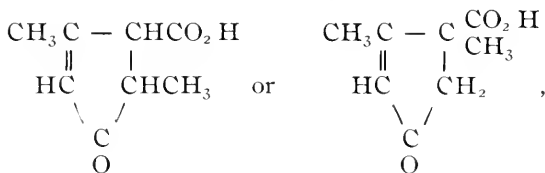
methronic ester,  $C_8 H_7 (C_2 H_5) O_5$ , a crystalline substance which melts at  $75^\circ$ - $76^\circ$ . The calcium, barium and silver salts were described. From it was prepared methronic acid,



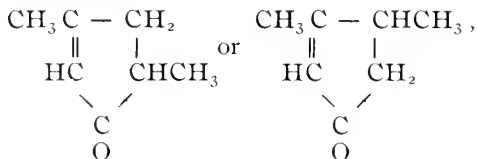
which decomposes at high temperatures to form uvic acid. Methronic diethyl ester,  $C_8 H_6 (C_2 H_5)_2 O_5$ , and a phenylhydrazin derivative were also described. By heating acetoacetic ester and pyruvic acid,  $CH_3 COCO_2 H$ , with acetic anhydrid, hydrogen methyl methronic ester is formed and from this the methyl-methronic acid which is



No acid salts of this are known but the normal calcium, barium and silver salts were described. Methyl-methronic diethyl ester was also described. From methyl-methronic acid were obtained methyl-uvic acid,



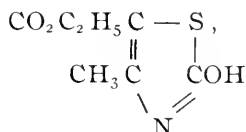
and dimethyl-keto-pentene,



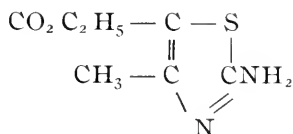
ZÜRCHER, H., 1889.

Ann. Chem. **250**, 281-294; J. Chem. Soc. **56**, 725; Ber. **22**, 258 (C).**Action of Thiocyanates and Thiocarbamids on Chlorinated Acetoacetic Esters.**

Methyl-oxythiazole-carboxylic ester,



is formed from monochlor-acetoacetic ester and a metallic thiocyanate. Some of its reactions and derivatives are described. Thiocarbamid acting on monochlor-acetoacetic ester gives amidomethyl-thiazole-carboxylic ester,



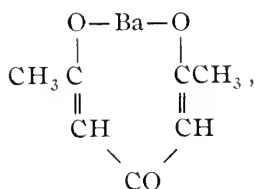
from which the free acid and some of its salts were obtained. Dichlor-acetoacetic ester reacts with barium thiocyanate to form a compound  $\text{C}_{14} \text{H}_{16} \text{O}_7 \text{N}_2 \text{S}_2$ . With thiocarbamid dichlor-acetoacetic ester does not react.

FEIST, FRANZ, 1889.

Ber. **22**, 1570-1571; J. Chem. Soc. **56**, 957; Bull. Soc. chim. [3] **3**, 657.**Dehydracetic Acid.**

Dehydracetic acid when treated with hydriodic acid gives dimethyl-pyrone,  $\text{CO} < \begin{array}{c} \text{CH} : \text{C}(\text{CH}_3) \\ \text{CH} : \text{C}(\text{CH}_3) \end{array} > \text{O}$ , which melts at  $132^\circ$ , boils at  $248^\circ$ - $249^\circ$

at 719 m. m. pressure. An aqueous solution of this gives with barium hydroxid  $C_7 H_8 O_3 Ba$  a (xantho) barium salt,



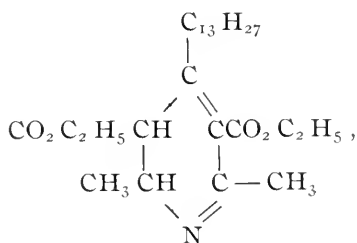
which, when treated with hydrochloric acid gives a tri-ketone  $CH_3 COCH_2 COCH_2 COCH_3$ , which melts at  $49^\circ$  and at higher temperatures gives off water and forms dimethyl-pyrone again. When the triketone is heated with ammonia, lutidone is formed.

#### KRAFFT, F. AND J. MAI, 1889.

Ber. **22**, 1757-1759; J. Chem. Soc. **56**, 1017.

#### Myristic Aldehyde.

When myristic aldehyde,  $C_{13} H_{27} CHO$ , ammonia and acetoacetic ester are mixed a reaction takes place and hydrotridecyl-lutidin-dicarboxylic ester,



is formed, which melts at  $60^\circ$ . From this were formed the corresponding compounds;—tridecyl-lutidin-di-carboxylic ester, tridecyl-lutidin-di-carboxylic acid and tridecyl-lutidin.

**SCHÖNBRODT, R., 1889.**

Ann. Chem. **253**, 168-205 ; J. Chem. Soc. **58**, 27 ; Ber. **22**, 680 (C).

**Derivatives of Acetoacetic Ester.**

By passing chlorin through cupracetoacetic ester in chloroform the mono- and di-chlor derivatives were formed and the corresponding bromin derivatives were similarly formed. Iodacetoacetic ester produced from cupracetoacetic ester and iodine is an unstable oil which decomposes at 25° in a vacuum, its specific gravity is 1.705 at 14°, in alcoholic solution it gives a blood red color with ferric chlorid. Silver chlorid converts it into mono-chlor-acetoacetic ester. When treated with silver nitrite an oil is produced which gives a blood red color with ferric chlorid and sulfuric acid and which is probably nitroacetoacetic ester. Treated with phenylhydrazin it gives phenyl-methyl-nitroso-pyrazolone [1 : 3 : 4 : 5]. Sodacetoacetic ester and iodacetoacetic ester give diacetosuccinic ester. Iodacetoacetic ester and metallic silver give



diacetofumaric ester,  $\text{CH}_3 \text{ COCCO}_2 \text{ R}$ . Cupracetoacetic ester boiled in

benzene with sulfur gives thioacetoacetic ester. In presence of alcohol, phosphorus acts on cupracetoacetic ester to form acetoacetic ester and tri-ethyl phosphite,  $\text{P}(\text{OC}_2\text{H}_5)_3$ . Cupracetoacetic ester and arsenic trichlorid form cuprous chlorid, arsenic and mono-chlor-acetoacetic ester. Unsuccessful attempts were made to replace hydrogen by copper in methyl-acetoacetic ester.

**GABRIEL, S. AND J. HAUSMANN, 1889.**

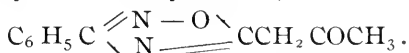
Ber. **22**, 2017-2019 ; J. Chem. Soc. **56**, 1172.

**Action of Orthocyanobenzylchlorid on Sodacetoacetic Ester.**

In this reaction two products are formed, a small amount of di-ortho-cyanobenzylacetoacetic ester,  $\text{CH}_3 \text{ COC}(\text{CNC}_6\text{H}_4\text{CH}_2)_2 \text{CO}_2 \text{C}_2\text{H}_5$ , and a much larger amount of orthocyanobenzylacetic ester, or orthocyanohydro-cinnamic ester,  $(\text{CNC}_6\text{H}_4\text{CH}_2) \text{CH}_2 \text{CO}_2 \text{C}_2\text{H}_5$ . The latter is a colorless, crystalline substance melting at 98°-99° which is decomposed when warmed with hydrochloric acid into  $\alpha$ -hydrindone, carbon dioxid, alcohol and ammonia.  $\alpha$ -Hydrindone,  $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CO} \\ \text{CH}_2 \end{smallmatrix} > \text{CH}_2$ , crystallizes and melts at 40° and boils at 243°-245°. Diortho-cyanobenzylacetoacetic ester is a colorless crystalline substance which melts at 120°.

**TIEMANN, F., 1889.**Ber. **22**, 2412-2417; J. Chem. Soc. **58**, 44.**Action of Acetaldehyde and Acetoacetic Ester on Benzenyl-amidoxim.**

Acetoacetic ester and benzenyl-amidoxim,  $\text{C}_6\text{H}_5\text{C} \begin{smallmatrix} \diagup \text{N} - \text{OH} \\ \diagdown \text{NH}_2 \end{smallmatrix}$ , react to form benzenylaceto-ethenylazoxim,



Alkalis decompose it, forming benzenyl-ethenyl-azoxim,



and acetic acid. The oxim,



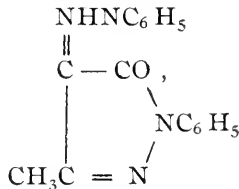
and the hydrazone,



were also described.

**BUCHKA, K. AND C. SPRAGUE, 1889.**Ber. **22**, 2541-2556; J. Chem. Soc. **58**, 28.**Thioacetoacetic Ester.**

This substance,  $\text{C}_{12}\text{H}_{18}\text{O}_6\text{S}$ , melts at  $76^\circ$  and forms a sodium derivative  $\text{C}_{12}\text{H}_{16}\text{Na}_2\text{O}_6\text{S}$ . Schönbrodt has proven that the sulfur is joined to the  $\alpha$ -carbon atom and not to oxygen. Phenylhydrazin reacts with it to form phenylmethyl-pyrazoloneketo-phenylhydrazone or phenylmethyl-pyrazolonazobenzene,



and a yellow substance which appears to be  $\text{C}_{10}\text{H}_8\text{N}_2\text{SO}$ . The compound which Schönbrodt describes as phenylmethyl-nitrosopyrazolone is identical with phenylmethyl-pyrazolonazobenzene. Thioacetoacetic ester unites with paratolylhydrazin and  $\alpha$ -naphthylhydrazin yielding a series of complicated compounds in each case.

**MICHAELIS, A. AND OSCAR BURCHARD, 1889.**Ann. Chem. **254**, 115-128.**Syntheses by Means of Sodium=phenylhydrazin. Ethylenphenyl=hydrazin.**

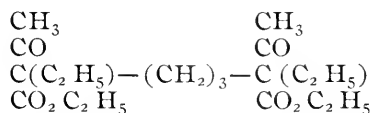
In the last paragraph of this article mention is made that ethylenphenylhydrazin easily condenses with acetoacetic ester to form a beautiful crystalline substance which melts at 54°. It is being investigated by the authors.

**RAYMAN, B. AND O. POHL, 1889.**Ber. **22**, 3247-3249; J. Chem. Soc. **58**, 355.**Rhamnodiazin.**

Rhamnodiazin,  $C_{18}H_{32}O_8N_2$ , is further studied but no very definite results are obtained. Its constitution is probably  $CH_3(CHOH)_4CH(N:C < \begin{smallmatrix} CH_3 \\ CH_2CO_2C_2H_5 \end{smallmatrix})_2$ . When rhamnose, acetoacetic ester and an amin are mixed they form rhamnosamin.

**KIPPING, F. STANLEY AND W. H. PERKIN, Jr., 1890.**J. Chem. Soc. **57**, 29-38; Ber. **23**, 249 (C). **$\alpha$ - $\omega$ -Diacetyl- $\alpha$ - $\omega$ -diethylpentane.**

This substance whose properties and reactions are described is obtained by treating sodacetoacetic ester with tri-methylene bromid. These substances combine to form  $\alpha$ - $\omega$ -diacetyl- $\alpha$ - $\omega$ -diethyl-pimelic ester which is



and when this is boiled with alcoholic potash there is formed  $\alpha$ - $\omega$ -diacetyl- $\alpha$ - $\omega$ -diethyl-pentane,  $CH_3COCH(C_2H_5)(CH_2)_3CH(C_2H_5)COCH_3$ , as well as some  $\omega$ -acetyl- $\alpha$ - $\omega$ -diethyl-caproic acid.

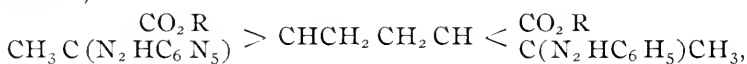
PERKIN, Jr., W. H., 1890.

J. Chem. Soc. **57**, 204-241.

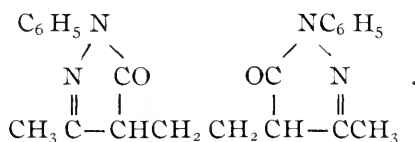
*α-α'*-Diacetyladipic Ester.

Sodacetoacetic ester and ethylene bromid react to form two products, (1) acetyl-trimethylene-carboxylic ester,  $\text{CH}_3\text{CO} > \text{C} < \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix}$ , and (2)

*α-α'*-diacetyladipic ester,  $\text{CH}_3\text{CO} > \text{CHCH}_2\text{CH}_2\text{CH} < \begin{smallmatrix} \text{COCH}_3 \\ | \\ \text{CO}_2\text{R} \end{smallmatrix}$ . The latter compound is a thick colorless oil, rather difficultly separable from impurities, which decomposes some when distilled yielding a mixture of several compounds. It will give a diphenylhydrazin derivative,



which melts at 145° and when heated higher gives bis-phenyl-methyl methylene-pyrazolone,



Many other reactions and derivatives of *α-α'*-diacetyladipic ester were given.

FEIST, FRANZ, 1890.

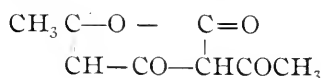
Ann. Chem. **257**, 253-297 ; Ber. **23**, 463 (C).

Dehydracetic Acid.

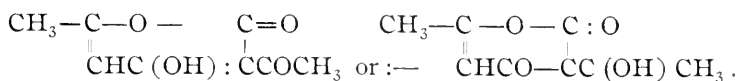
In this long article account is given of a study of dehydracetic acid made in order to determine its constitutional formula and its relation to its isomers. A large number of reactions are described and a great many of its derivatives are produced and their constitution determined. A figure is given representing the most important reactions and a table



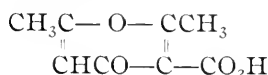
of comparisons of the three isomeric bodies  $C_8H_8O_4$ . They are assigned the following formulæ. For dehydracetic :—



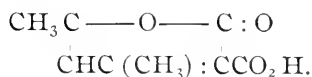
or the tautomeric forms of :—



For  $\alpha$ - $\alpha$ -dimethyl-pyrone-carboxylic acid :—



and for isodehydracetic acid :—



### PETERS, THEODOR, 1890.

Ann. Chem. **257**, 339-353 ; J. Chem. Soc. **58**, 1097 ; Ber. **23**, 468 (C).

#### Action of Alkyl Substituted Acetoacetic Esters with Ammonia.

By the action of ammonia on these esters two products are formed (1)  $\alpha$ -alkyl- $\beta$ -amido-crotonic acid,  $CH_3C(NH_2) : CRCO_2R$ , and (2) amids of alkylacetoacetic acid,  $CH_3COCHRCONH_2$ , but the former only is produced when anhydrous ammonia is employed. Ethyl-acetoacetic methyl ester yields ethyl-amido-crotonic methyl ester,  $CH_3C(NH_2) : C(C_2H_5)CO_2CH_3$ , which melts at  $35^\circ$ - $36^\circ$ , and ethyl-acetoacetamid,  $CH_3COCH(C_2H_5)CONH_2$ , melting at  $96^\circ$ . Methyl-acetoacetic ester yields methyl-acetoacetamid,  $CH_3COCH(CH_3)CONH_2$ , melting at  $73^\circ$ .  $\alpha$ -Methyl- $\beta$ -amido-crotonic ester melts at  $53^\circ$ . Isobutyl acetoacetamid melts at  $88^\circ$ ,  $\alpha$ -isobutyl- $\beta$ -amido-crotonic ester melts at  $41^\circ$ - $42^\circ$ , isoamyl-acetoacetamid,  $CH_3COCH(C_5H_{11})CONH_2$ , melts at  $129^\circ$  and  $\alpha$ -isoamyl- $\beta$ -amido-crotonic ester,  $CH_3C(NH_2) : C(C_5H_{11})CO_2C_2H_5$ , melts at  $50^\circ$ . Diethyl-acetoacetic ester is not attacked by either anhydrous or aqueous ammonia.

**PETERS, THEODOR, 1890.**

Ann. Chem. **257**, 353-358; J. Chem. Soc. **58**, 1096; Ber. **23**, 468 (C).

**Action of Alcohols on Acetoacetic Ester.**

When a little sodium is dissolved in the alcohol, methyl, isopropyl and isoamyl alcohols will convert acetoacetic ester into the methyl, isopropyl and isoamyl esters respectively, slowly at ordinary temperatures but quickly if heated. Even in the absence of sodium, isopropyl and isoamyl alcohols will thus convert acetoacetic ester if the mixtures be boiled together, while methyl alcohol has no action in the absence of sodium. Ethyl-acetoacetic ester reacts similarly with these alcohols. Acetoacetic isobutyl ester,  $\text{CH}_3\text{COCH}_2\text{CO}_2\text{C}_4\text{H}_9$ , boils at  $198^\circ\text{--}202^\circ$  and its ethyl derivative,  $\text{CH}_3\text{COCH}(\text{C}_2\text{H}_5)\text{CO}_2\text{C}_4\text{H}_9$ , boils at  $211^\circ\text{--}215^\circ$ . Acetoacetic isoamyl ester,  $\text{CH}_3\text{COCH}_2\text{CO}_2\text{C}_5\text{H}_{11}$ , boils at  $217^\circ\text{--}219^\circ$  and its ethyl derivative,  $\text{CH}_3\text{COCH}(\text{C}_2\text{H}_5)\text{CO}_2\text{C}_5\text{H}_{11}$ , boils at  $226^\circ\text{--}230^\circ$ .

**MICHAELIS, A. AND B. PHILIPS, 1890.**

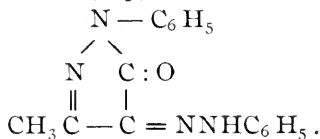
Ber. **23**, 559-561; J. Chem. Soc. **58**, 582.

**Thio-acetoacetic Ester.**

This substance was prepared by treating acetoacetic ester with thionyl chlorid,  $\text{SOCl}_2$ ; it melts at  $100^\circ\text{--}101^\circ$ . When treated with an excess of phenylhydrazin it gives phenylmethylpyrazolonazobenzene which melts at  $156^\circ$ , but when twice the molecular proportion of phenylhydrazin is added in cold, acetic acid a compound of the composition  $\text{C}_{20}\text{H}_{22}\text{N}_4\text{O}_4\text{S}$  is produced. This is probably thioacetoacetic phenylhydrazid which is

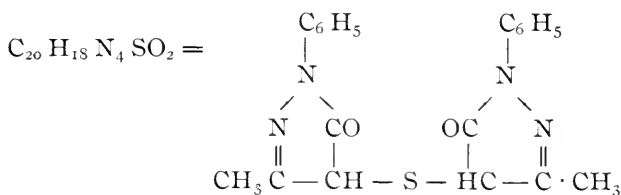


it decomposes at  $185^\circ$ . When this is heated with an excess of phenylhydrazin it forms phenylmethyl pyrazolonazobenzene,

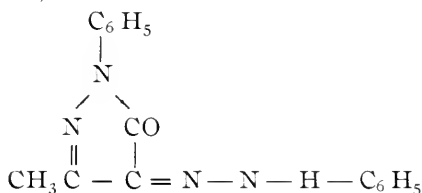


**BUCKA, K. AND CH. SPRAGUE, 1890.**Ber. **23**, 847-855 ; J. Chem. Soc **58**, 796.**Action of Phenylhydrazin on Thioacetoacetic Ester.**

When these substances react in cold, glacial acetic acid in the proportion of one molecule of thioacetoacetic ester to two molecules of phenylhydrazin they form thiophenylmethylpyrazolone,



and not  $\text{C}_{20}\text{H}_{22}\text{N}_4\text{SO}_4$  as Michaelis and Philips state in their article (\*which see). It decomposes at  $183^\circ$  without melting, is soluble in alkalis and forms stable salts with strong acids. When heated with an excess of phenylhydrazin it goes over into phenylmethylpyrazolone-ketophenylhydrazone which is the same as Michaelis' phenyl-methyl-pyrazolonazobenzene,

**CLOEZ, C., 1890.**Compt. rend. **110**, 583-586 ; J. Chem. Soc. **58**, 739 ; Ber. **23**, 284 (C).**Hydroxytetric Acid.**

By treating methyl-acetoacetic ester with bromin dibrom-methyl-acetoacetic ester,  $\text{C}_6\text{H}_7\text{Br}_2(\text{CH}_3)\text{O}_3$ , is formed, and when this is treated with alcoholic potash, hydroxytetric acid,  $\text{C}_5\text{H}_6\text{O}_4$ , is obtained,

\* See page 116.

which melts at  $201^{\circ}$ – $202^{\circ}$ . By the action of water on dibrom-methyl-acetoacetic ester in presence of barium chlorid hydroxytetric ester,  $C_5H_5(C_2H_5)O_4$ , is obtained, it melts at  $67^{\circ}$ – $68^{\circ}$  and has an acid reaction. By treating an alcoholic solution of hydroxytetric acid with gaseous hydrochloric acid a body boiling at  $224^{\circ}$ – $226^{\circ}$  and having the composition of hydroxytetric diethyl ester is obtained.

**CLOEZ, C., 1890.**

Bull. Soc. chim. [3] **3**, 602–605; Ber. **23**, 435 (C).

**Identity of Hydroxytetric and Mesaconic Acids.**

The author proves the identity of these acids by their melting points, solubility in water, volatilization, brown color given with ferric chlorid and the same reactions towards bromin and acetyl chlorid.

**HALLER, A. AND A. HELD, 1890.**

Compt. rend. **III**, 647–650; J. Chem. Soc. **60**, 171.

**$\gamma$ -Cyanacetoacetic Esters and their Chlor-imido Derivatives.**

$\gamma$ -Cyanacetoacetic ester boils at  $135^{\circ}$  to  $138^{\circ}$ , at 40 to 45 m.m. pressure, with some decomposition. Treated with hydrochloric acid in alcoholic solution the hydrochlorid of the imido ester of acetone-dicarboxylic ester,  $CH_2(CO_2C_2H_5)COCH_2C(OC_2H_5)(NH), HCl$ , is formed which is very unstable being decomposed by water.  $\gamma$ -Cyanacetoacetic methyl ester boils at  $217^{\circ}$  to  $218^{\circ}$  and when treated with hydrochloric acid in methyl alcohol it yields the hydrochlorid of the imido ester of acetondicarboxylic methyl ester + one molecule of HCl which is either  $CH_2(CO_2CH_3)CH(OH)CHClC(OCH_3)(NH), HCl$  or  $CHCl(CO_2CH_3)CH(OH)CH_2C(OCH_3)(NH), HCl$ .

NEF, J. U., 1890.

Ann. Chem. **258**, 261-318, Am. Chem. J. **12**, 379-425; J. Chem. Soc. **58**, 983.

### Tautomeric Compounds.

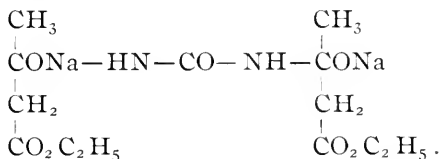
In this article acetoacetic ester is considered and the author decides that it is a tautomeric compound; that the sodium derivative has the sodium combined to oxygen, thus:  $\text{CH}_3\text{CONa}:\text{CHCO}_2\text{C}_2\text{H}_5$ , but that the ester itself and its alkyl derivatives have the ketonic oxygen, thus:  $\text{CH}_3\text{COCHRCO}_2\text{R}$ . By treating sodacetoacetic ester with benzoyl chlorid two compounds were produced, the principal one was monobenzoyl-acetoacetic ester and the minor one was dibenzoyl-acetoacetic ester,  $\text{CH}_3\text{COC}(\text{COC}_6\text{H}_5)_2\text{CO}_2\text{C}_2\text{H}_5$ , which has never been prepared before. It is very unstable and cannot be distilled even in vacuum.

BEHREND, R. AND PAUL ERNERT, 1890.

Ann. Chem. **258**, 360-362; J. Chem. Soc. **58**, 1240; Ber. **23**, 643(C).

### Condensation of Carbamid with Acetoacetic Ester.

Carbamid condenses with sodacetoacetic ester to form a compound  $\text{C}_{13}\text{H}_{22}\text{N}_2\text{O}_7\text{Na}_2$  which is probably represented by the formula

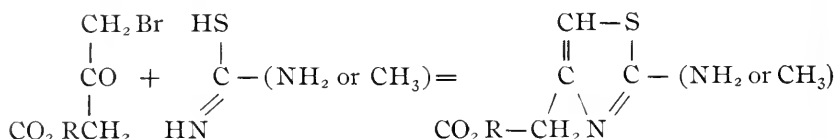


It melts at  $165^\circ$  and is decomposed by water. It is also decomposed, by passing carbon dioxid into its alcohol solution, into carbamid, acetoacetic ester and sodium ethyl carbonate,  $\text{NaC}_2\text{H}_5\text{CO}_3$ .

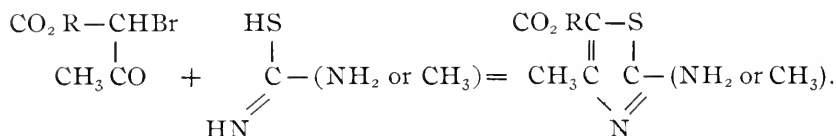
## HANTZSCH, A., 1890.

Ber **23**, 2339-2342; J. Chem. Soc. **58**, 1238.**Halogen Derivatives of Acetoacetic Ester.**

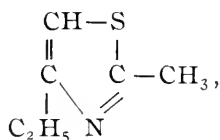
The action of thiocarbamid and thioacetamid on the halogen derivatives of acetoacetic ester are used to distinguish between the  $\alpha$  and  $\gamma$  positions for the halogen thus:



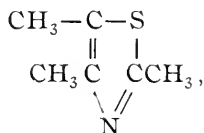
which is amido- or methyl- thiazylacetic ester and



Bromin acting on acetoacetic ester gives the  $\gamma$  product but when cupracetoacetic ester is treated with bromin the  $\alpha$  product is obtained. Chlorin acting on acetoacetic ester gives the  $\alpha$  product. Methyl-ethyl-thiazole,



was produced from methyl-brom-acetoacetic ester showing it to be the  $\gamma$  product and trimethyl-thiazole,



was produced from methyl-chlor-acetoacetic ester showing it to be the  $\alpha$  derivative.

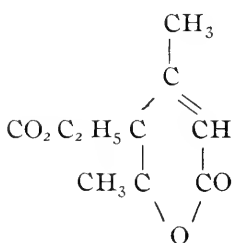
**DITTRICH, E., 1890.**Ber. **23**, 2720-2725; J. Chem. Soc. **58**, 1418.**Action of Picric Chlorid on Sodacetoacetic Ester.**

By the action of picric chlorid,  $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{Cl}$ , on sodacetoacetic ester the mono- or di- trinitrophenyl-acetoacetic ester is formed, according to the proportion of picric chlorid used. Trinitrophenyl-acetoacetic ester,  $\text{CH}_3\text{COCH}[\text{C}_6\text{H}_2(\text{NO}_2)_3]\text{CO}_2\text{C}_2\text{H}_5$ , melts at  $98^\circ$ , dissolves in alkalis from which solution weak acids precipitate it. Di- (trinitrophenyl) acetoacetic ester,  $\text{CH}_3\text{COC}[\text{C}_6\text{H}_2(\text{NO}_2)_3]_2\text{CO}_2\text{C}_2\text{H}_5$ , melts at  $205^\circ$  with decomposition; alcoholic potash dissolves it and acids precipitate not the same but trinitrophenyl-acetoacetic ester. When trinitrophenyl-acetoacetic ester is boiled with sulfuric acid trinitrophenyl acetone,  $\text{CH}_3\text{COCH}_2[\text{C}_6\text{H}_2(\text{NO}_2)_3]$ , is formed which melts at  $89^\circ$ . This condenses with phenylhydrazin to  $\text{C}_{15}\text{H}_{13}\text{N}_5\text{O}_6$ , which melts with decomposition at  $125^\circ$ .

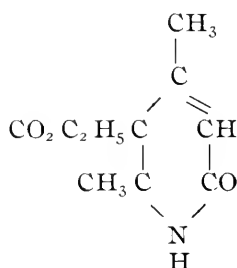
**ANSCHÜTZ, R., P. BENDIX AND W. KERP, 1890.**Ann. Chem. **259**, 148-186; J. Chem. Soc. **60**, 172; Ber **23**, 734 (C).**Mesitene Lactone and Isodehydracetic Acid,**

Much of the work done by Hantzsch on the condensation products of acetoacetic ester has been repeated by the authors. They corroborate his formulæ for mesitene lactone and isodehydracetic acid,  $(\text{C}_8\text{H}_8\text{O}_4)$ , but find that the first condensation product is a mixture of isodehydracetic acid and its ethyl ester. Isodehydracetic methyl ester melts at  $67^\circ$  and boils at  $167^\circ$  under 14 m.m. pressure, it can be obtained by treating the potassium salt with methyl iodid or by condensing acetoacetic methyl ester. Unsuccessful attempts were made to prepare Hantzsch's homomesaconic acid; by treating isodehydracetic ester with potash two acids were obtained; (1)  $\text{C}_{10}\text{H}_{12}\text{O}_4$  which melts with decomposition at  $221^\circ$ , is almost insoluble in ether, benzene, chloroform and cold water and but moderately soluble in boiling water. Its potassium, barium and copper salts and methyl ester were described. The second

acid  $C_8H_{10}O_3$ , melts at  $149^\circ$ , is soluble in alcohol, ether and chloroform and decomposes at  $160^\circ$ ; its barium and silver salts were described. Isodehydracetic ester is converted by warm anhydrous ammonia into the corresponding lactam, identical with the substance obtained by Collie by the condensation of  $\beta$ -amido-crotonic ester. The change is represented thus :

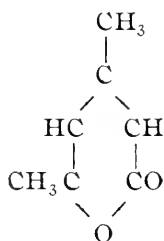


Isodehydracetic ester

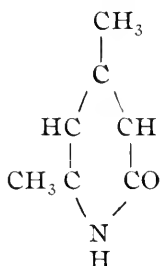


Caroxethylmesiteulactam.

Mesitene lactone



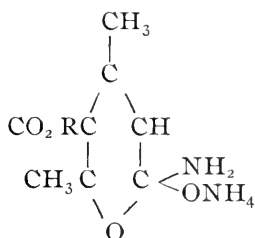
is changed by ammonia into mesitene lactam



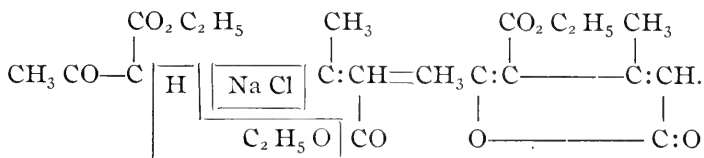
An alcoholic ethereal solution of isodehydracetic ester treated in the



cold with ammonia forms a compound  $C_{10}H_{18}N_2O_4$ , if moisture be excluded. It is represented thus:—



Isodehydracetic ester can be prepared from sodacetoacetic ester and  $\beta$ -chlorcrotonic ester which proves its constitution thus:—



AUTENRIETH, W., 1890.

Ann. Chem **259**, 365-373 ; J. Chem. Soc. **60**, 204.

### Sulfur Derivatives of Acetoacetic, Methylacetoacetic and Ethylacetoacetic Esters.

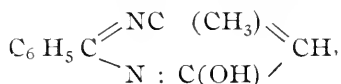
By treating  $\beta$ -dithiophenylbutyric ester,  $\text{CH}_3\text{C}(\text{SC}_6\text{H}_5)_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$ , with sulfuric acid and potassium permanganate,  $\beta$ -diphenylsulfonebutyric ester,  $\text{CH}_3\text{C}(\text{SO}_2\text{C}_6\text{H}_5)_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$ , is obtained, it melts at  $97^\circ$ , is soluble in hot alcohol, ether and benzene and insoluble in water.  $\alpha$ -Ethyl- $\beta$ -diethylsulfonebutyric ester,  $\text{CH}_3\text{C}(\text{SO}_2\text{C}_2\text{H}_5)_2\text{CH}(\text{C}_2\text{H}_5)\text{CO}_2\text{C}_2\text{H}_5$ , formed in a similar manner from the condensation product of ethyl mercaptan and ethyl-acetoacetic ester, melts at  $87^\circ$ - $88^\circ$ .  $\alpha$ -Methyl- $\beta$ -diethylsulfonebutyric ester melts at  $79^\circ$ .  $\alpha$ -Ethyl- $\beta$ -dithiophenylbutyric ester,  $\text{CH}_3\text{C}(\text{SC}_6\text{H}_5)_2\text{CH}(\text{C}_2\text{H}_5)\text{CO}_2\text{C}_2\text{H}_5$ , is made by condensing ethyl-acetoacetic ester and phenyl mercaptan, and melts at  $70^\circ$ - $71^\circ$ . From this by the above method was prepared  $\alpha$ -ethyl- $\beta$ -diphenylsulfonebutyric ester,  $\text{CH}_3\text{C}(\text{SO}_2\text{C}_6\text{H}_5)_2\text{CH}(\text{C}_2\text{H}_5)\text{CO}_2\text{C}_2\text{H}_5$ , which melts at  $111^\circ$ .

**ELION, H., 1890.**Ber. **23**, 3123-3124; J. Chem. Soc. **60**, 171.**Preparation and Properties of Sodacetoacetic and Sod-ethylacetoactic Esters.**

Both these substances when anhydrous are soluble in ether but both form hydrous compounds insoluble in ether. The anhydrous compounds cannot be obtained by keeping the hydrous compounds over sulfuric acid as has been stated and the author thinks that there is but one form of anhydrous sodacetoacetic ester and not two, one of which is insoluble in ether as stated by Michael.

**PINNER, A., 1890.**Ber. **23**, 3820-3826; J. Chem. Soc. **60**, 468.**Imido Esters and their Derivatives.**

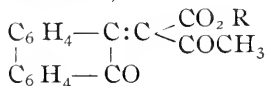
Acetoacetic ester is treated with imidobenzoic ester and the chief product is found to be phenylmethyl-hydroxypyrimidin,



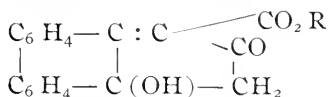
melting at 216°. The imidobenzoic ester is probably first converted into benzoic ester and ammonia thus:  $\text{C}_6\text{H}_5\text{C}(\text{NH})\text{OC}_2\text{H}_5 + \text{H}_2\text{O} = \text{C}_6\text{H}_5\text{CO}_2\text{C}_2\text{H}_5 + \text{NH}_3$ ; the ammonia acts on some imido-benzoic ester forming alcohol and benzamidin which last product unites with the acetoacetic ester.

**JAPP, FRANCIS R. AND FELIX KLINGEMANN, 1891.**J. Chem. Soc. **59**, 1-26.**Phenanthroxylene-acetoacetic Ester.**

This compound, prepared from acetoacetic ester and phenanthraquinone and given the formula,



has been further studied. When treated with formic or sulfuric acid an isomer is formed, to which the formula,



is provisionally given, and which is called isophenanthroxylene-acetoacetic ester; it melts at  $177^\circ$ . It forms a mono-acetyl derivative,  $\text{C}_{20}\text{H}_{15}(\text{C}_2\text{H}_3\text{O})\text{O}_4$ , which melts between  $165^\circ$  and  $170^\circ$ , and a mono-hydrazone,  $\text{C}_{20}\text{H}_{16}\text{O}_3(\text{N}_2\text{HC}_6\text{H}_5)$ . No pyrazolone could be obtained from this, and phenanthroxylene-acetoacetic ester does not react with phenylhydrazin. With bromin the iso compound gave  $\text{C}_{20}\text{H}_{15}\text{BrO}_4$ . When reduced the iso compound gave  $\text{C}_{20}\text{H}_{16}\text{O}_3$ , which is also produced from the phenanthroxylene-acetoacetic ester by means of hydriodic acid. This gave a phenylhydrazin derivative,  $\text{C}_{20}\text{H}_{16}\text{O}_2(\text{N}_2\text{HC}_6\text{H}_5)$ . When treated with hydriodic acid the iso compound gave  $\text{C}_{17}\text{H}_{12}\text{O}$ , which is the compound to which Japp and Streatfield\* gave the formula  $\text{C}_{14}\text{H}_{10}\text{O}$ . It is probably a ketone containing the carbonyl group in a penta-carbon ring. Treated with an alkali the iso compound gave the iso-phenanthroxylene-acetoacetic acid,  $\text{C}_{18}\text{H}_{12}\text{O}_4$ , which is mono-basic. The action of acetic, propionic, sulfuric, alcoholic hydrochloric acids and of alcoholic potash and ammonia on phenanthroxylene-acetoacetic ester was determined and an account given of the experiments. The subject requires more study before the composition of these bodies can be definitely settled. The formula proposed for the iso compound explains some reactions but leaves others quite unexplained.

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\* See page 39.

### CLAISEN, L. AND E. HORI, 1891.

Ber. **24**, 139-140; J. Chem. Soc. **60**, 416.

#### Action of Hydroxylamin on Acetoacetic Aldehyde.

By this action a compound  $\text{C}_8\text{H}_{13}\text{N}_3\text{O}_3$ , was produced which crystallizes in white needles, melting at  $174^\circ$ . It is sparingly soluble in ether, benzene and chloroform. Other compounds which were expected from this reaction were not obtained.

## EMERY, W. O., 1891.

Ber. **24**, 282-286 ; J. Chem. Soc. **60**, 547.**Action of  $\beta$ -Bromopropionic Ester on Acetoacetic Ester.**

By the action of  $\beta$ -bromopropionic ester on sodacetoacetic ester,

$\alpha$ -acetylglutaric ester,  $\begin{array}{c} \text{CH}_3 \\ \text{CO} \\ \text{CH} - \text{CH}_2 - \text{CH}_2 \text{CO}_2 \text{C}_2 \text{H}_5, \end{array}$  was produced. It

boils at  $162^\circ$  at 11 m. m. pressure and has a specific gravity of 1.071 at  $20^\circ$ . It reacts with ammonia and with amines, yielding amido-derivatives of  $\alpha$ -ethylidineglutaric ester, which can be converted into lactams.

## HANTZSCH, A., 1891.

Ber. **24**, 495-506 ; J. Chem. Soc. **60**, 739.**Action of Hydroxylamin on  $\beta$ -Ketonic Acids and  $\beta$ -Diketones.**

By the action of hydroxylamin on acetoacetic ester in alkaline solution and subsequent acidification the chief product is methyl-isoxazolone,

one,  $\text{CH}_3 \text{C} \begin{array}{l} \nearrow \text{N} - \text{O} \\ \searrow \text{CH}_2 \text{CO} \end{array}$ , which melts at  $169^\circ - 170^\circ$  and is a base towards

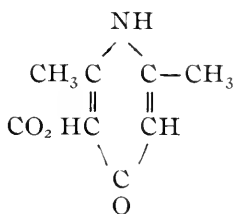
strong acids. In alkaline solutions it is partially changed into oximido-butyric acid,  $\text{CH}_3 \text{C} : (\text{NOH}) \text{CH}_2 \text{CO}_2 \text{H}$ . By the action of hydroxylamin on acetoacetic ester in neutral or acid solution, an oil is obtained which, on being hydrolyzed, gives a crystalline substance,  $\text{C}_{20} \text{H}_{26} \text{N}_4 \text{O}_7$ , which melts at  $140^\circ$  and can by hydrolysis be changed into methyl-isoxazolone. By the action of hydroxylamin on acetoacetic ester in ammoniacal solution an unstable product was obtained which may be

the hydroxamic acid of acetoacetic acid,  $\text{CH}_3 \text{COCH}_2 \text{C} \begin{array}{l} \nearrow \text{OH} \\ \searrow \text{NOH} \end{array}$ .

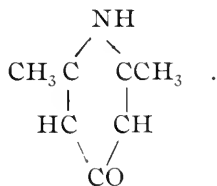
COLLIE, J. NORMAN, 1891.

J. Chem. Soc. **59**, 172-179.**Action of Heat on  $\beta$ -Amidocrotonic Ester.**

When this substance is distilled a small amount of substance is always left which has been found to be  $C_{10}H_{13}NO_3$ , the ethyl ester of an acid,  $C_8H_9NO_3$ , which is dimethyl-pyridone-monocarboxylic acid,



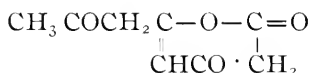
The ester,  $C_{10}H_{13}NO_3$ , melts at  $163^\circ$ - $164^\circ$  and boils with slight decomposition at  $240^\circ$  to  $250^\circ$ . It does not form a compound with phenylhydrazin or hydroxylamin. With bromin it forms  $C_{10}H_{12}BrNO_3$ ; with  $PCl_5$  it gives  $C_{10}H_{12}NO_2Cl$ , which can be changed into chlorolutidin boiling at  $177^\circ$  to  $180^\circ$ . The acid  $C_8H_9NO_3$ , melts at  $257^\circ$ - $258^\circ$  and is converted into  $\alpha$ - $\alpha'$ -dimethyl-pyridone,



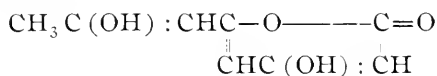
This was also prepared from dehydracetic acid. Phosphorus pentachlorid acts on  $\alpha$ - $\alpha'$ -dimethyl-pyridone to form chlorolutidin boiling at  $178^\circ$ - $179^\circ$ .  $\alpha$ - $\alpha'$ -Dimethyl-pyridin or lutidin was obtained in four ways, (1) by the action of nascent hydrogen on chlorolutidin; only a little could be formed in this way; (2) from vapors of chlorolutidin and zinc dust in an atmosphere of hydrogen; (3) from chlorolutidin made from dehydracetic acid; (4) from the potassium salt of lutidone-monocarboxylic acid heated with an excess of solid potassium hydroxid. By oxidation of the lutidin, dipicolinic acid,  $C_5H_3N(CO_2H)_2$ , was obtained.

**COLLIE, J. NORMAN, 1891.**J. Chem. Soc. **59**, 179-189.**Constitution of Dehydracetic Acid.**

The author, having studied this acid and its reactions, determines that Feist\* did not present the correct formula for it and proposes the formula

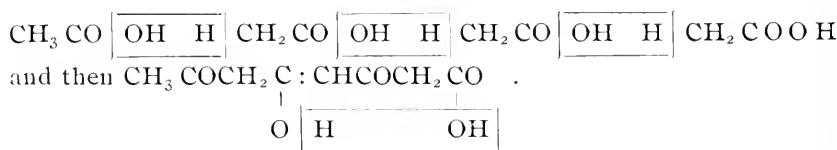


or the tautomeric form

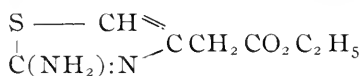


By this formula he thinks that all of its reactions, the most important ones of which he illustrates, can best be explained. He considers it as

built up on the nucleus of  $\alpha$ -oxypyrrone,  $\begin{array}{c} \text{CH} - \text{O} - \text{CO} \\ \parallel \\ \text{CH} - \text{CO} - \text{CH}_2 \end{array}$ . Its formation from acetic acid is illustrated thus:—

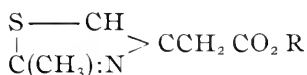
**STEUDE, M., 1891.**Ann. Chem. **261**, 22-47; J. Chem. Soc. **60**, 742**Thiazole Derivatives from Bromacetoacetic Ester.**

The thiazole derivatives obtained from bromacetoacetic ester and thio-carbamid and thiacetamid are isomeric with those obtained if chloracetoacetic ester be used, but those obtained both ways can be converted into  $\mu$ -amido- $\alpha$ -methyl-thiazole or  $\alpha$ - $\mu$ -dimethyl-thiazole as the case may be. This proves that bromacetoacetic ester has the formula  $\text{CH}_2 \text{BrCOCH}_2 \text{CO}_2 \text{R}$ .  $\mu$ -Amido-thiazylacetic ester,



\* See page 114.

obtained from bromacetoacetic ester and thiocarbamid melts at 94°, the free acid melts at 130°. Thiacetamidoacetic ester,  $\text{CH}_2(\text{SCNHCH}_3)\text{COCH}_2\text{CO}_2\text{C}_2\text{H}_5$ , is formed besides  $\mu$ -methyl-thiazylacetic ester from bromacetoacetic ester and thiacetamid in alcoholic solution. Methyl-thiazylacetic ester,



boils at 238° to 240°.  $\gamma$ -Thiacetoacetoacetic ester,  $\text{CH}_2(\text{SCOCH}_3)\text{COCH}_2\text{CO}_2\text{R}$ , results when thiacetamidacetoacetic ester hydrobromid is warmed with water. It boils at 155° at 15 m. m. pressure. A compound, probably of the formula  $\text{CO}_2\text{RCH}_2\text{C} \begin{smallmatrix} \nearrow \text{CH} - \text{S} \\ \searrow \text{SCH} \end{smallmatrix} \parallel \text{CCH}_2\text{CO}_2\text{R}$ , was also described.

### PECHMANN, H. v. AND M. DÜNSCHMANN, 1891.

Ann. Chem. **261**, 162-166; J. Chem. Soc. **60**, 672.

#### Decomposition of Acetone-dicarboxylic Ester.

When acetone-dicarboxylic ester,  $\text{CO}_2\text{C}_2\text{H}_5\text{CH}_2\text{COCH}_2\text{CO}_2\text{C}_2\text{H}_5$ , is changed to the potassium salt and then boiled with water, acetoacetic ester is produced which is identified by being treated with phenylhydrazin and changed into methyl-phenylpyrazolone.

### JAEGER, J., 1891.

Ann. Chem. **262**, 365-372; J. Chem. Soc. **60**, 1007.

#### Condensation of Guanidin with $\beta$ -Ketonic Esters.

Guanidin carbonate and acetoacetic ester condense to form imido-methyl-uracyl,  $\text{CH} \begin{smallmatrix} \nearrow \text{CO NH} \\ \searrow \text{C}(\text{CH}_3)\text{NH} \end{smallmatrix} > \text{C}:\text{NH}$ , which melts with decomposition at 270°. The hydrochlorid, nitrate and sulfate were described. Dibromohydroxyimidomethyl-uracyl,  $\text{NH} \begin{smallmatrix} \nearrow \text{C}(\text{NH})\text{NH} \\ \searrow \text{COC}(\text{Br}_2) \end{smallmatrix} > \text{CCH}_3\text{OH}$ , is formed together with bromimidomethyluracyl,  $\text{C}_5\text{H}_6\text{BrN}_3\text{O}$ , when imidomethyl-uracyl is heated with bromin; it melts at 160°. When

imidomethyluracyl is heated with an excess of methyl iodid a compound,  $(C_5 H_6 N_3 O CH_3)_2 HI$ , is obtained, which melts at  $212^\circ$  and can be converted into methyl-imidomethyl-uracyl,  $C_5 H_6 N_3 OCH_3$ , which melts at  $312^\circ$ . Imidodimethyluracyl formed from guanidiu carbonate and methyl-acetoacetic ester melts at  $320^\circ$ , and imido-phenyl-uracyl formed from guanidin carbonate and benzoylacetic ester melts at  $294^\circ$ .

**BREDT, J., 1891.**

Ber. **24**, 603-605; J. Chem. Soc. **60**, 712.

**Action of Sodacetoacetic Ester on Benzalmalonic Ester.**

By this reaction in alcoholic solution at 0 a crystalline sodium compound is formed which when decomposed by an acid gives a compound  $C_{18} H_{20} O_6$ , which is sparingly soluble in water and melts with decomposition at  $155^\circ$ .

**OTTO, R. AND A. RÖSSING, 1891.**

Ber. **24**, 685-687; J. Chem. Soc. **60**, 712.

**Action of Sodium Phenylmercaptid on Chloracetoacetic Ester.**

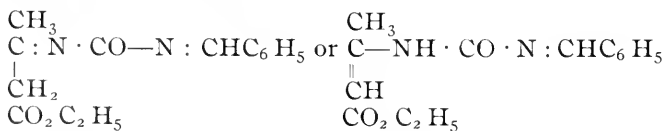
When equivalent quantities of these substances are made to react in alcoholic solutions, an oil is obtained, which will not crystallize and has but a feeble odor. It appears to be thiophenylacetoacetic ester,  $CH_3 COCH (SC_6 H_5) CO_2 C_2 H_5$ .

**BIGINELLI, P., 1891.**

Ber. **24**, 1317-1319; J. Chem. Soc. **60**, 908.

**Aldehydeuramids of Acetoacetic Ester. Part 1.**

Molecular proportions of acetoacetic ester, benzaldehyde and carbamid are allowed to react and a crystalline compound melting at  $207^\circ$ - $208^\circ$  is obtained. It is either





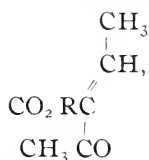
but probably is the latter. The same substance can be formed from uramidocrotonic ester and benzaldehyde. It is very stable as it is not affected by strong acids or alkalis in the cold. Heating it with potassium hydroxid gives benzyl alcohol, benzaldehyde, ammonia and potassium carbonate, besides an unknown solid substance. Salicylaldehyde, cinnamaldehyde, furfuraldehyde, cumaldehyde and others react similarly.

### BEYER, C., 1891.

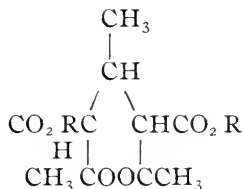
Ber **24**, 1662-1670; J. Chem. Soc. **60**, 1090.

#### Hantzsch's Pyridin Synthesis,

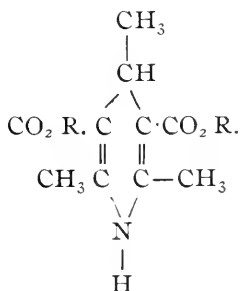
The author believes that in these reactions acetoacetic ester and aldehyde first react to form ethylidin-acetoacetic ester,



and that this then unites with acetoacetic ester to form ethylidin-diacetoacetic ester,



which unites with ammonia to form dihydrocollidin-dicarboxylic ester,



Ethylidinacetoacetic ester and paramido-acetoacetic ester were mixed in molecular proportions and united to form dihydrocollidin-dicarboxylic ester. Several other experiments were performed and several pyridin derivatives made and described. They all agreed with these reactions.

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**FREER, P. C., 1891.**

Am. Chem. J. **13**, 308-322; J. Chem. Soc. **60**, 1181.

**Constitution of Aliphatic Ketones and the Action of Sodium on Acetone.**

The constitution of acetoacetic ester is discussed at length and mention is made of the work done by different chemists upon it. Acetic ester dried over calcium chlorid and by being boiled over phosphorus pentoxid is found to react with sodium readily which inclines the author to believe in the intermediate sodacetic ester. A comparison of the properties and reactions of tetric acid and acetoacetic ester seems to show that the former contains a hydroxyl group and the latter does not. In the sodium derivative the author believes the sodium is joined to the oxygen, therefore that its constitution is different from that of acetoacetic ester itself. This is shown by the fact that sodacetoacetic ester will form addition products with unsaturated compounds like cinnamic ester while the acetoacetic ester itself will not.

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**FREER, PAUL C. AND GEO. O. HIGLEY, 1891.**

Am. Chem. J. **13**, 322-326; J. Chem. Soc. **60**, 1182.

**Action of Chlorcarbonic Ester on Acetone Sodium.**

By this action a colorless oil boiling at about 125° was obtained which appears to be an isomer of acetoacetic ester. It is insoluble in water, miscible with alcohol and ether and does not react with phenyl hydrazin or ferric chlorid. On boiling with hydro chloric acid it is decomposed into carbon dioxid, alcohol and acetone. The authors suggest for it

the formula  $\begin{array}{c} \text{CH}_2 \\ \text{CH}_3 \end{array} \text{C} = \text{C} - \text{O} - \text{CO}_2 \text{C}_2 \text{H}_5$ .

## WALDEN, P., 1891.

Ber. 24, 2025-2039; J. Chem. Soc. 60, 1187.

**Tetric and Oxytetric Acids and their Homologues.**

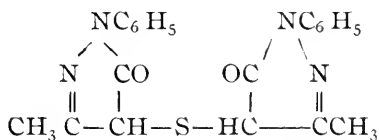
Experiments were performed attempting to determine whether tetric acid and its homologues contain the carboxylic group but no definite conclusions were reached. Oxytetric acid and its homologues were shown to be alkyl substituted fumaric acids, thus oxytetric is mesaconic or methyl fumaric, oxypentic is ethyl fumaric, etc. The acids described by Demarcay as hydroxytetric, etc., are identical with alkyl succinic acids, hydroxytetric is methyl succinic and hydroxypentic is ethyl succinic, etc. The acids are all obtained from the bromated alkyl aceto-acetic esters.

## SPRAGUE, CHARLES T., 1891.

J. Chem. Soc. 59, 329-343.

**Thiacetoacetic Ester.**

This substance was produced and after carefully determining the melting point it was found to be between 75° and 78°. By the action of phenylhydrazin four bodies were produced:—(1) thiophenyl-methyl-pyrazolone; (2) Knorr's phenylmethyl-pyrazolone-azobenzene; (3) a substance,  $C_{10}H_9^*N_2SO$ ; (4) Knorr's bisphenyl-methyl-pyrazolone. The first one is



it is a weak base, dissolves in alkalis and weak acids reprecipitate it. If it be heated with phenylhydrazin the other three above mentioned compounds are produced. To the third product the author gave the formula  $C_{10}H_8^*N_2SO$ , but states that Höltzcka has since proven it to be bisulphid of phenylmethyl pyrazolone  $(C_{10}H_9N_2O)_2S_2$ . A method was given for preparing a good yield of each one of the four products.

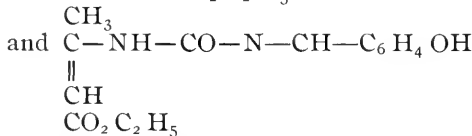
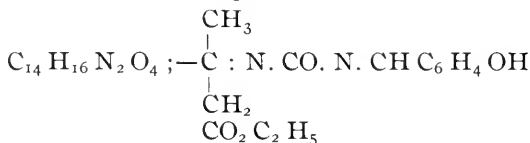
\* A disagreement,  $C_{10}H_8N_2SO$  is probably correct

**COLLIE, J. NORMAN, 1891.**J. Chem. Soc. **59**, 617-621.**Some Reactions of Dehydracetic Acid.**

In the preparation of dehydracetic acid by passing acetoacetic ester through a red-hot iron tube, there were formed, besides the dehydracetic acid, acetone, alcohol, carbon dioxid, ethylene and a residue. Acetoacetic methyl ester similarly treated gave large quantities of dehydracetic acid, but ethylacetoacetic ester gave none at all. Dehydracetic acid is slightly decomposed by water into carbon dioxid and dimethylpyrone. When boiled with hydrochloric acid it is totally decomposed into carbon dioxid and a compound,  $C_7H_{11}O_3Cl$ , which melts at 83-85 and is acid in water solution. Barium and copper salts of dehydracetic acid were prepared, the former corresponded most nearly with  $(C_8H_9O_5)_2Ba$  and was considered to be the salt of tetracetic acid,  $CH_3COCH_2COCH_2COCH_2CO_2H$ ; and the latter corresponded to  $C_{24}H_{25}O_9N_3Cu$ , being formed by ammonia and copper acetate. Hydrocyanic acid has no action on dehydracetic acid.

**BIGINELLI, P., 1891.**Ber. **24**, 2962-2967; J. Chem. Soc. **62**, 56.**Aldehydeuramids of Acetoacetic Ester. Part II.**

In the continuation of the subject it is found that two isomers, corresponding to the two formulæ given in the first article on this subject,\* are always produced. The compounds



formed from carbamid, salicylaldehyde and acetoacetic ester, and the similar compounds,  $C_{17}H_{22}N_2O_3$ , formed from cumaldehyde,  $C_6H_4(C_3H_7)COH$ , carbamid and acetoacetic ester;  $C_{16}H_{18}N_2O_3$ , obtained by using cinnamaldehyde, and  $C_{12}H_{14}N_2O_4$ , obtained by using furfuraldehyde, are produced and described.

\* See page 130.

CONRAD, M. AND L. LIMPACH, 1891.

Ber. 24, 2990-2992, J. Chem. Soc. 62, 78.

**Synthesis of Quinolin Derivatives by means of Alkyl Acetoacetic Esters.**

Methyl-acetoacetic methyl ester and anilin, when mixed and allowed to stand, form phenyl-amido-methyl-crotonic methyl ester. By quickly heating this, it is changed into dimethyl-hydroxyquinolin,  $C_9NH_4(CH_3)_2OH$ ,  $[(CH_3)_2 : OH = 2' : 3' : 4']$ . Methyl-ethyl-hydroxy-quinolin is produced similarly from phenyl-amido-ethyl-crotonic methyl ester.

NEF, J. U., 1891.

Ann. Chem. 266, 52-138; J. Chem. Soc. 62, 140.

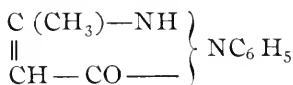
**Acetoacetic Ester.**

A large number of experiments are performed relative to determining the constitution of acetoacetic ester and the position of the sodium in the sodium derivative, and the conclusions drawn are that acetoacetic ester is not a ketone but is represented by  $CH_3COH : CHCO_2C_2H_5$  and that in the sodium derivative the sodium is joined to oxygen. If by heating the sodacetoacetic ester with an alkyl halogen the alkyl is substituted for the sodium, the reaction should be more energetic if the heavier metals, such as copper or lead, be in the acetoacetic ester in place of sodium, but solutions of the copper or lead derivatives of acetoacetic ester do not react with ethyl iodid at ordinary temperatures—which proves that no direct substitution of the metal takes place. The author supposes an intermediate addition product to be formed with an alkyl iodid, for example, with benzylchlorid,  $CH_3CONaClCH(CH_2C_6H_5)CO_2R$  is first formed and then HCl splits off leaving  $CH_3CONa : C(CH_2C_6H_5)CO_2R$  and by continued action  $CH_3CONaClC(CH_2C_6H_5)_2CO_2R$  and then  $CH_3COC(CH_2C_6H_5)_2CO_2R$  are formed. As proof of the existence of hydroxyl in acetoacetic ester its acid properties and its behavior towards phenyl hydrazin, ammonia and the amids are mentioned, also the fact that acetoacetic ester and its mono-alkyl derivatives are not reduced by treatment with sodium in ethereal solution while the diethyl derivative is converted into

diethyl-hydroxybutyric ester. The substitution of the  $\alpha$ -hydrogen atom affects the compound according to the character of the substituted group, making it more alcoholic or more acidic as that group is more or less positive than hydrogen. By the action of phenylhydrazin on acetoacetic ester phenyl- $\beta$ -hydrazo-crotonic ester,  $\text{CH}_3 \text{C} (\text{N}_2 \text{H}_2 \text{C}_6 \text{H}_5) : \text{CHCO}_2 \text{R}$ , melting at  $50^\circ$  is formed and by heating this with mercuric oxid phenyl- $\beta$ -azocrotonic ester,  $\text{CH}_3 \text{C} (\text{N}_2 \text{C}_6 \text{H}_5) : \text{CHCO}_2 \text{R}$ , melting at  $51^\circ$  is obtained. The product obtained by the action of bromin on acetoacetic is a mixture of the  $\alpha$  and the  $\gamma$  brom-derivatives.  $\alpha$ -Brom-methyl-acetoacetic ester,  $\text{C}_7 \text{H}_{11} \text{Br O}_3$ , boiling at  $107^\circ$  at 30 m.m. pressure, is obtained by treating sodmethyl-acetoacetic ester or methyl-acetoacetic ester with bromin. When this is heated in a sealed tube tetric acid is formed for which the author gives the formula



$\alpha$ -Bromethylacetoacetic ester,  $\text{C}_8 \text{H}_{13} \text{Br O}_3$ , is prepared similarly and is described. Dibenzoyl-acetoacetic ester,  $\text{C}_{20} \text{H}_{18} \text{O}_5$ , and triacetylacetic ester,  $\text{CH}_3 \text{CO C} (\text{CH}_3 \text{CO})_2 \text{CO}_2 \text{R}$ , and acetylcarbintricarboxylic ester,  $\text{CH}_3 \text{CO C} (\text{CO}_2 \text{R})_2 \text{CO}_2 \text{R}$ , are also described. A large number of pyrazolone derivatives are prepared and studied, and the author decides that their acid properties are due to the presence of an imido group. The formula for phenylmethyl-pyrazolone he gives as




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#### PECHMANN, H. v., 1891.

Ber. **24**, 3600; J. Chem. Soc. **62**, 296.

#### Preparation of Dehydracetic Acid.

By treating acetondicarboxylic acid with acetic anhydrid, a substance either isomeric or identical with the carboxylic acid of dehydracetic acid is produced. This may be easily changed into dehydracetic acid by dissolving in soda, evaporating to dryness and precipitating the aqueous solution with acetic acid.

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INDEXES

TO THE

LITERATURES OF CERIUM  
AND LANTHANUM

BY

W. H. MAGEE, PH. D.



CITY OF WASHINGTON  
PUBLISHED BY THE SMITHSONIAN INSTITUTION

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## LETTER OF TRANSMITTAL.

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The Committee of the American Association for the Advancement of Science having charge of Indexing Chemical Literature has voted to recommend to the Smithsonian Institution for publication the three following Indexes:—

AN INDEX TO THE LITERATURE OF CERIUM.

AN INDEX TO THE LITERATURE OF LANTHANUM.

Both by W. H. Magee, Ph. D.

AN INDEX TO THE LITERATURE OF DIDYMIUM.<sup>1</sup>

By A. C. Langmuir, Ph. D.

The latter has already appeared in the *School of Mines Quarterly*, No. 1, Vol. XV.

H. CARRINGTON BOLTON,

*Chairman.*

To the SECRETARY of the SMITHSONIAN INSTITUTION.

<sup>1</sup> This Index is printed as Smithsonian Publication No. 972.



# INDEXES TO THE LITERATURES OF CERIUM AND LANTHANUM.

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By W. H. MAGEE, PH. D.

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## INTRODUCTION.

THE following indexes to the literatures of cerium and lanthanum were prepared during the course of some work on the former element. They are not offered as being absolutely correct, but all the more important articles bearing upon the elements are certainly indexed, and usually the original article heads the list. In some few cases, however, it was difficult to determine the original. Whenever the journal was to be found on the library shelves the references were verified. No single library, however, contains all the journals to which references will be found.

That the indexing of chemical literature is of great and growing importance is evident; that the work should be as nearly perfect as possible is equally true. Yet few except those who have attempted the task realize the difficulty and labor involved. I would ask, therefore, as regards these indexes, that any one using them, and all chemists interested in the study of cerium and lanthanum, should send corrections and addenda to W. H. Magee, care of Professor L. M. Dennis, Cornell University, Ithaca, N. Y., so that after a few years perfectly correct indexes may be prepared.

The Indexes are arranged on the same plan as that of the Index to Uranium, published by Dr. H. Carrington Bolton in 1870, and followed by several other chemists. The abbreviations used are in the main those of the standard list printed in Bolton's Bibliography of Chemistry.

CORNELL UNIVERSITY,  
ITHACA, N. Y., July 21, 1894.





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INDEX

TO THE

LITERATURE OF DIDYMIUM

1842-1893

BY

A. C. LANGMUIR, PH. D.



CITY OF WASHINGTON  
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## LETTER OF TRANSMITTAL.

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AN INDEX TO THE LITERATURE OF DIDYMIUM.

By A. C. Langmuir, Ph. D.

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# INDEX TO THE LITERATURE OF DIDYMIUM — 1842-1893.

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BY A. C. LANGMUIR, PH. D.

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THE following paper is offered to chemists with the hope that it may be of some value to them in their researches on an element of great theoretical and scientific interest, particularly as an example of the wonderful results accomplished by the use of the spectroscope in modern chemistry. The voluminous literature of didymium affords a striking illustration of the pursuit of science for its own sake, and with no reward beyond the satisfaction of having advanced the cause of truth.

Original work, at the present time, must always be preceded by a long and painstaking search through the literature, which consumes no inconsiderable amount of time. Anything which can lighten the labors of the investigator in this direction is sure to be a welcome addition to the literature.

In 1882 Dr. H. Carrington Bolton originated the idea of indexing the literature of each of the chemical elements, and a Committee on Indexing Chemical Literature was appointed by the American Association for the Advancement of Science. The committee annually reports the progress made during the year, the reports being published in the *Chemical News* and in American journals.

The following elements have been indexed : —

*Columbium*. — Index to the literature of, 1801-1887, by Frank W. Traphagen, Smithsonian Miscellaneous Collections, No. 663, Washington, 1888.

- Iridium*.—Bibliography of the metal, 1803-1885, by N. W. Perry, in Mineral Resources of the United States, 1883-1884, p. 588; School of Mines Quarterly, 1885, p. 114; Chem. News, 1885, 51, p. 32.
- Manganese*.—Index to the literature of, 1596-1874, by H. C. Bolton, Annals of the Lyceum of Natural History, New York, Vol. II., Nov., 1875.
- Titanium*.—Index to the literature of, 1783-1876, by E. J. Hallock, Annals of the New York Academy of Sciences, Vol. I., Nos. 2 and 3, 1877.
- Uranium*.—Index to the literature of, by H. C. Bolton, 1789-1885, Smithsonian Reports for 1885, Washington, 1885, p. 919-946.
- Vanadium*.—Index to the literature of, 1801-1876, by G. Jewett Rockwell, Annals of the New York Academy of Sciences, Vol. I., No. 5, 1877.

The general plan of the following index corresponds with that of the others published. The indexes at the end of every volume of each journal were consulted, unless an index covering a series of years was available. The French journals proved to be very troublesome in this respect, as indexes at the end of the volume are often omitted, and the general indexes are seldom detailed enough to be of much value. This was especially true of the *Bull. Soc. Chim.* and the *Ann. Chim. Phys.*

The abbreviations used are those given by H. Carrington Bolton in his "Select Bibliography of Chemistry, 1492-1892," Smithsonian Miscellaneous Collections, No. 840, Washington, 1893.

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1843	MOSANDER . . .	Researches.	Phil. Mag. [3], 23, 241. Ann. Chem., Liebig, 48, 210-223. J. prakt. Chem., 30, 276-288. Ann. de Phys., Pogg., 60, 299-311. Ann. chim. phys. [3], 11, 464.
1843	L. BONAPARTE .	Separation from cerium.	Compt. rend., 16, 1008. J. prakt. Chem., 29, 268. Pharm. Centrbl., 1843, 719. Berzelius' Jsb., 1845, 115. Ann. der Phys., Pogg., 59, 623. Chem. Gaz., 1843, 405. Chemist, Watt, 4, 293. Am. J. Sci., 46, 206.
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1850	H. WATTS . . . .	Sep'r'tion fr'm cerium and lanthanum.	J. Chem. Soc., 2, 140. Pharm. Centrbl., 1849, 892.
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1857	GLADSTONE . . .	Optical test.	J. Chem. Soc., 10, 219. J. prakt. Chem., 73, 380. Am. J. Sci. [2], 25, 100. Jsb., 1857, 568.
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1861	NORDENSKIÖLD . . . . .	Crystalline form of oxide.	Ann. der Phys., Pogg., 114, 618. Oefvers. K. Vet. Acad. Forhandl., 1860, 439.
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1864	POPP . . . . .	Separation from cerium.	Ann. Chem., Liebig, 131, 359. Bull. soc. chim., 3, 385.
1864	BUNSEN . . . . .	Absorption spectrum.	Ann. Chem., Liebig, 131, 255. Arch. ph. nat., 21, 384. Phil. Mag. [4], 28, 246. Jsb., 1864, 108.
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SMITHSONIAN MISCELLANEOUS COLLECTIONS

— 1075 —

THE CONSTANTS OF NATURE  
PART V  
A RECALCULATION  
OF  
THE ATOMIC WEIGHTS

BY

FRANK WIGGLESWORTH CLARKE

*Chief Chemist of the U. S. Geological Survey*

NEW EDITION, REVISED AND ENLARGED



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1897

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## ADVERTISEMENT.

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The present publication is one of a series devoted to the discussion and more precise determination of various "Constants of Nature;" and forms the Fifth contribution to that subject published by this Institution.

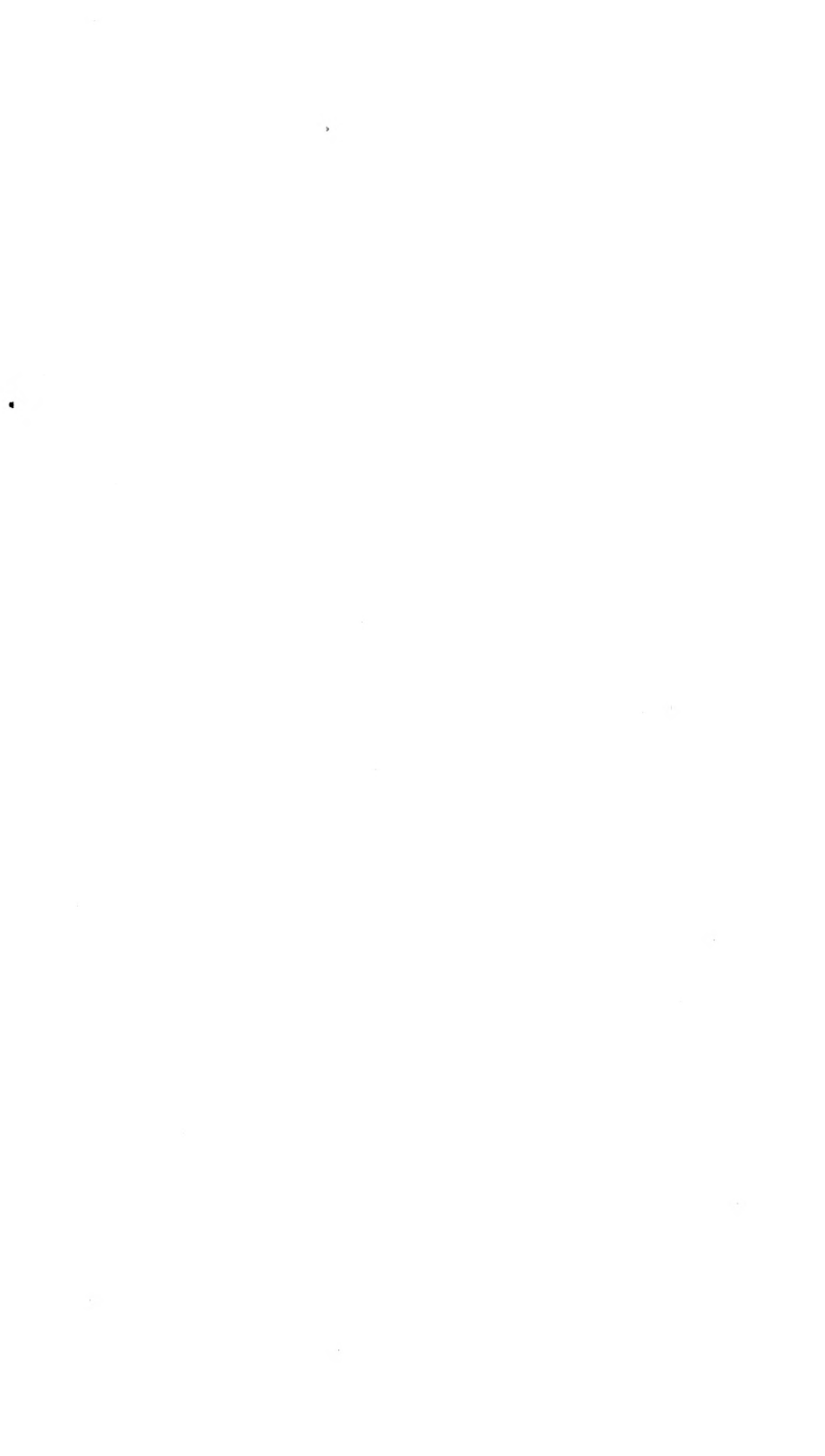
The First number of the series, embracing tables of "Specific Gravities" and of Melting and Boiling Points of Bodies, prepared by the same author, Prof. F. W. Clarke, was published in 1873. The Fourth part of the series, comprising a complete digest of the various "Atomic Weight" determinations of the chemical elements published since 1814, commencing with the well-known "Table of Equivalents" by Wollaston (given in the Philosophical Transactions for that year), compiled by Mr. George F. Becker, was published by the Institution in 1880. The present work comprises a very full discussion and recalculation of the "Atomic Weights" from all the existing data, and the assignment of the most probable value to each of the elements.

The first edition of this work was published in 1882, and this new edition, revised and enlarged by Professor Clarke, contains new information accumulated during the past fifteen years.

S. P. LANGLEY,

*Secretary of the Smithsonian Institution.*

WASHINGTON, *January, 1897.*



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# A RECALCULATION OF THE ATOMIC WEIGHTS.

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By FRANK WIGGLESWORTH CLARKE. .

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## INTRODUCTION.

In the autumn of 1877 the writer began collecting data relative to determinations of atomic weight, with the purpose of preparing a complete résumé of the entire subject, and of recalculating all the estimations. The work was fairly under way, the material was collected and partly discussed, when I received from the Smithsonian Institution a manuscript by Professor George F. Becker, entitled "Atomic Weight Determinations: a Digest of the Investigations Published since 1814." This manuscript, which has since been issued as Part IV of the "Constants of Nature," covered much of the ground contemplated in my own undertaking. It brought together all the evidence, presenting it clearly and thoroughly in compact form; in short, that portion of the task could not well be improved upon. Accordingly, I decided to limit my own labors to a critical recalculation of the data; to combine all the figures upon a common mathematical basis, and to omit everything which could as well be found in Professor Becker's "Digest."

In due time my work was completed, and early in 1882 it was published. About a year later Meyer and Seubert's recalculation appeared, to be followed later still by the less elaborate discussions of Sebelien and of Ostwald. All of these works differed from one another in various essential particulars, presenting the subject from different points of view, and with different methods of calculation. Each one, therefore, has its own special points of merit, and, in a sense, reinforces the others. At the same time, the scientific activity which they represent shows how widespread was the interest in the subject of atomic weights, and how fundamentally important these constants undoubtedly are.

The immediate effect of all these publications was to render manifest the imperfections of many of the data, and to point out most emphatically in what directions new work needed to be done. Consequently, there has been since 1884 an extraordinary activity in the determination of atomic weights, and a great mass of new material has accumulated. The assimilation of this material, and its combination with the old data, is the object of the present volume.

At the very beginning of my work, certain fundamental questions confronted me. Should I treat the investigations of different individuals separately, or should I combine similar data together in a manner irrespective of persons? For example, ought I, in estimating the atomic weight of silver, to take Stas' work by itself, Marignac's work by itself, and so on, and then average the results together; or should I rather combine all series of figures relating to the composition of potassium chlorate into one mean value, and all the data concerning the composition of silver chloride into another mean, and, finally, compute from such general means the constant sought to be established? The latter plan was finally adopted; in fact, it was rendered necessary by the method of least squares, which, in a special, limited form, was chosen as the best method of dealing with the problem.

The mode of discussion and combination of results was briefly as follows. The formulæ employed are given in another chapter. I began with the ratio between oxygen and hydrogen; in other words, with the atomic weight of oxygen referred to hydrogen as unity. Each series of experiments was taken by itself, its arithmetical mean was found, and the probable error of that mean was computed. Then the several means were combined according to the appropriate formula, each receiving a weight dependent upon its probable error. The general mean thus established was taken as the most probable value for the atomic weight of oxygen, and, at the same time, its probable error was mathematically assigned.

Next in order came a group of elements which were best discussed together, namely, silver, chlorine, potassium, sodium, bromine, and iodine. For these elements there were data from many experimenters. All similar figures were first reduced to common standards, and then the means of individual series were combined into general means. Thus all the data were condensed into nineteen ratios, from which several independent values for the atomic weight of each element could be computed. The probable errors of these values, however, all involved the probable error of the atomic weight of oxygen, and were, therefore, higher than they would have been had the latter element not entered into consideration. Here, then, we have suggested a chief peculiarity of this whole revision. The atomic weight of each element involves the probable errors of all the other elements to which it is directly or indirectly referred. Accordingly, an atomic weight determined by reference to elements whose atomic weights have been defectively ascertained will receive a high probable error, and its weight, when combined with other values, will be relatively low. For example, an atomic weight ascertained by direct comparison with hydrogen will, other things being equal, have a lower probable error than one which is referred to hydrogen through the intervention of oxygen; and a metal whose equivalent involves only the probable error of oxygen should be more exactly

known than one which depends upon the errors of silver and chlorine. These points will appear more clearly evident in the subsequent actual discussions.

But although the discussion of atomic weights is ostensibly mathematical, it cannot be purely so. Chemical considerations are necessarily involved at every turn. In assigning weights to mean values I have been, for the most part, rigidly guided by mathematical rules; but in some cases I have been compelled to reject altogether series of data which were mathematically excellent, but chemically worthless because of constant errors. In certain instances there were grave doubts as to whether particular figures should be included or rejected in the calculation of means, there having been legitimate reasons for either procedure. Probably many chemists would differ with me upon such points of judgment. In fact, it is doubtful whether any two chemists, working independently, would handle all the data in precisely the same way, or combine them so as to produce exactly the same final results. Neither would any two mathematicians follow identical rules or reach identical conclusions. In calculating the atomic weight of any element those values are assigned to other elements which have been determined in previous chapters. Hence a variation in the order of discussion might lead to slight differences in the final results.

As a matter of course the data herein combined are of very unequal value. In many series of experiments the weighings have been reduced to a vacuum standard; but in most cases chemists have neglected this correction altogether. In a majority of instances the errors thus introduced are slight; nevertheless they exist, and interfere more or less with all attempts at a theoretical consideration of the results.

Necessarily, this work omits many details relative to experimental methods, and particulars as to the arrangement of special forms of apparatus. For such details original memoirs must be consulted. Their inclusion here would have rendered the work unwarrantably bulky. There is such a thing as over-exhaustiveness of treatment, which is equally objectionable with under-thoroughness.

Of course, none of the results reached in this revision can be considered as final. Every one of them is liable to repeated corrections. To my mind the real value of the work, great or little, lies in another direction. The data have been brought together and reduced to common standards, and for each series of figures the probable error has been determined. Thus far, however much my methods of combination may be criticised, I feel that my labors will have been useful. The ground is cleared, in a measure, for future experimenters; it is possible to see more distinctly what remains to be done; some clues are furnished as to the relative merits of different series of results.

On the mathematical side my method of recalculation has obvious deficiencies. It is special, rather than general, and at some future time, when a sufficiently large mass of evidence has accumulated, it must

give way to a more thorough mode of treatment. For example, the ratio  $\text{Ag}_2 : \text{BaBr}_2$  has been used for computing the atomic weight of barium, the atomic weights of silver and bromine being supposed to be known. But these atomic weights are subject to small errors, and they are superimposed upon that of the ratio itself in the process of calculation. Obviously, the ratio should contribute to our knowledge of all three of the atomic weights involved in it, its error being distributed into three parts instead of appearing in one only. The errors may be in part compensatory; but that is not certainly known.

Suppose now that for every element we had a goodly number of atomic weight ratios, connecting it with at least a dozen other elements, and all measured with reasonable accuracy. These hundreds of ratios could then be treated as equations of observation, reduced to linear form, and combined by the general method of least squares into normal equations. All errors would thus be distributed, never becoming cumulative; and the normal equations, solved once for all, would give the atomic weights of all the elements simultaneously. The process would be laborious but the result would be the closest possible approach to accuracy. The data as yet are inadequate, although some small groups of ratios may be handled in that way; but in time the method is sure to be applied, and indeed to be the only general method applicable. Even if every ratio was subject to some small constant error, this, balanced against the similar errors of other ratios, would become accidental or unsystematic with reference to the entire mass of material, and would practically vanish from the final means.

Concerning this subject of constant and accidental errors, a word may be said here. My own method of discussion eliminates the latter, which are removable by ordinary averaging; but the constant errors, vicious and untractable, remain, at least partially. Still, where many ratios are considered, even the systematic errors may in part compensate each other, and do less harm than might be expected. They have, moreover, a peculiarity which deserves some attention.

In the discussion of instrumental observations, the systematic errors are commonly constant, both as to direction and as to magnitude. They are therefore independent of the accidental errors, and computation of means leaves them untouched. But in the measurement of chemical ratios the constant errors are most frequently due to an impurity in one of the materials investigated. If different samples of a substance are studied, although all may contain the same impurity, they are not likely to contain it in the same amount; and so the values found for the ratio will vary. In other words, such errors may be constant in direction but variable in magnitude. That variation appears in the probable error computed for the series of observations, diminishes its weight when combined with other series, and so, in part, corrects itself. It is not removed from the result, but it is self-mitigated. The constant errors familiar to the physicist and astronomer are obviously of a different order.



That all methods of averaging are open to objections, I am of course perfectly aware. I also know the doubts which attach to all questions of probable error, and to all combinations of data which depend upon them. I have, however, preferred to face these objections and to recognize these doubts rather than to adopt any arbitrary scheme which permits of a loose selection of data. After all, the use of probable error as a means of weighting is but a means of weighting, and perhaps more justifiable than any other method of attaining the same result. When observations are weighted empirically—that is, by individual judgment—far greater dangers arise. Almost unconsciously, the work of a famous man is given greater weight than that of some obscure chemist, although the latter may ultimately prove to be the best. But the probable error of a series of measurements is not affected by the glamor of great names; and the weight which it assigns to the observations is at least as safe as any other. In the long run, I believe it assigns weight more accurately, and therefore I have trusted to its indications, not as if it were a mathematical fetish, but regarding it as a safe guide, even though sometimes fallible.

In Meyer and Seubert's recalculation, weights are assigned in quite a novel manner. In each series of experiments the maximum and minimum results are given, but instead of the mean there is a value deduced from the sum of the weighings—that is, each experiment is weighted proportionally to the mass of the material handled in it. For this method I am unable to find any complete justification. Of course, the errors due to the operations of weighing become proportionally smaller as the quantity of material increases, but these errors, with modern apparatus, are relatively unimportant. The real errors in atomic weight determinations are much larger than these, and due to different causes. Hence an experiment upon ten grammes of material may be a little better than one made upon five grammes, but it is by no means necessarily twice as good. The ordinary mean of a series of observations, with its measure of concordance, the probable error, is a better value than one obtained in the manner just described. If only errors of weighing were to be considered, Meyer and Seubert's summation method would be valid, but in the presence of other and greater errors it seems to have but little real pertinency to the problem at hand.

In addition to the usual periodicals, the following works have been freely used by me in the preparation of this volume:

BERZELIUS, J. J. *Lehrbuch der Chemie*. 5 Auflage. Dritter Band. SS. 1147–1231. 1845.

VAN GEUNS, W. A. J. *Proeve eener Geschiedenis van de Æquivalentgetallen der Scheikundige Grondstoffen en van hare Soortelijke Gewigten in Gasvorm, voornamelijk in Betrekking tot de vier Grondstoffen der Werktuigde Natuur*. Amsterdam, 1853.

- MULDER, E. Historisch-Kritisch Overzicht van de Bepalingen der Æquivalent-Gewigten van 13 Eenvoudige Ligchamen. Utrecht, 1853.
- MULDER, L. Historisch-Kritisch Overzicht van de Bepalingen der Æquivalent-Gewigten van 24 Metalen. Utrecht, 1853.
- OUDEMANS, A. C., Jr. Historisch-Kritisch Overzicht van de Bepaling der Æquivalent-Gewigten van Twee en Twintig Metalen. Leiden, 1853.
- STAS, J. S. Untersuchungen über die Gesetze der Chemischen Proportionen über die Atomgewichte und ihre gegenseitigen Verhältnisse. Uebersetzt von Dr. L. Aronstein. Leipzig, 1867.  
See also his "Oeuvres Complètes," 3 vols., published at Bruxelles in 1894.
- MEYER, L., and SEUBERT, K. Die Atomgewichte der Elemente, aus den Originalzahlen neu berechnet. Leipzig, 1883.
- SEBELIEN, J. Beiträge zur Geschichte der Atomgewichte. Braunschweig, 1884.
- OSTWALD, W. Lehrbuch der allgemeinen Chemie. Zweite Aufl. I Band. SS. 18-138. Leipzig, 1891.

The four Dutch monographs above cited are especially valuable. They represent a revision of all atomic weight data down to 1853, as divided between four writers.

For the sake of completeness the peculiar volume by Hinrichs\* must also be cited, although the methods and criticisms embodied in it have not been generally endorsed. Hinrichs' point of view is so radically different from mine that I have been unable to make use of his discussions. His objections to the researches of Stas seem to be quite unfounded; and the rejoinders by Spring and by Van der Plaats are sufficiently thorough.

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\* The True Atomic Weight of the Chemical Elements and the Unity of Matter. St. Louis, 1894. Compare Spring, Chem. Zeitung, Feb. 22, 1893, and Van der Plaats, Compt. Rend., 116, 1362. See also a paper by Vogel, with adverse criticisms by Spring and L. Henry, in Bull. Acad. Bruxelles, (3), 26, 469.

## FORMULÆ FOR THE CALCULATION OF PROBABLE ERROR.

The formula for the probable error of an arithmetical mean, familiar to all physicists, is as follows :

$$(1.) \quad e = 0.6745 \sqrt{\frac{S}{n(n-1)}}$$

Here  $n$  represents the number of observations or experiments in the series, and  $S$  the sum of the squares of the variations of the individual results from the mean.

\* In combining several arithmetical means, representing several series, into one general mean, each receives a weight inversely proportional to the square of its probable error. Let  $A, B, C$ , etc., be such means, and  $a, b, c$  their probable errors respectively. Then the general mean is determined by the formula :

$$(2.) \quad M = \frac{\frac{A}{a^2} + \frac{B}{b^2} + \frac{C}{c^2} \dots \dots}{\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2} \dots \dots}$$

For the probable error of this general mean we have :

$$(3.) \quad e = \frac{1}{\sqrt{\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2} \dots \dots}}$$

In the calculation of atomic and molecular weights the following formulæ are used: Taking, as before, capital letters to represent known quantities, and small letters for their probable errors respectively, we have for the probable error of the sum or difference of two quantities,  $A$  and  $B$  :

$$(4.) \quad e = \sqrt{a^2 + b^2}$$

For the product of  $A$  multiplied by  $B$  the probable error is

$$(5.) \quad e = \sqrt{(Ab)^2 + (Ba)^2}$$

For the product of three quantities,  $ABC$  :

$$(6.) \quad e = \sqrt{(BCa)^2 + (ACb)^2 + (ABc)^2}$$

For a quotient,  $\frac{B}{A}$ , the probable error becomes

$$(7.) \quad e = \frac{\sqrt{\left(\frac{Ba}{A}\right)^2 + b^2}}{A}$$

Given a proportion,  $A : B :: C : x$ , the probable error of the fourth term is as follows:

$$(8.) \quad e = \frac{\sqrt{\left(\frac{BCa}{A}\right)^2 + (Cb)^2 + (Bc)^2}}{A}$$

This formula is used in nearly every atomic weight calculation, and is, therefore, exceptionally important. Rarely a more complicated case arises in a proportion of this kind:

$$A : B :: C + x : D + x$$

In this proportion the unknown quantity occurs in two terms. Its probable error is found by this expression, and is always large:

$$(9.) \quad e = \sqrt{\frac{(C-D)^2}{(A-B)^4} (B^2a^2 + A^2b^2) + \frac{B^2c^2 + A^2d^2}{(A-B)^2}}$$

When several independent values have been calculated for an atomic weight they are treated like means, and combined according to formulæ (2) and (3). Each final result is, therefore, to be regarded as the general or weighted mean of all trustworthy determinations. This method of combination is not theoretically perfect, but it seems to be the one most available in practice.

## OXYGEN.

The ratio between oxygen and hydrogen is the foundation upon which the entire system of atomic weights is sustained. Hence, the accuracy of its determination has, from the beginning, been recognized as of extreme importance. A trifling error here may become cumulative when repeated through a moderate series of other ratios. But few of the elements have, so far, been compared directly with the unit, hydrogen; practically all of them are referred to it through the intervention of oxygen, and therefore the ratio in question requires discussion before any other can be profitably considered.

Leaving out of account the earliest researches, which now have only historical value, the first determinations to be noted are those of Dulong and Berzelius,\* who, like some of their successors, effected the synthesis of water over heated oxide of copper. The essential features of the method are in all cases the same. Hydrogen gas is passed over the hot oxide, and the water thus formed is collected and weighed. From this weight and the loss of weight which the oxide undergoes, the exact com-

\* Thomson's Annals of Philosophy, July, 1821, p. 50.

position of water is readily calculated. Dulong and Berzelius made but three experiments, with the following results for the percentages of oxygen and hydrogen in water:

O.	H.
88.942	11.058
88.809	11.191
88.954	11.046

From these figures we get, for the atomic weight of oxygen, the values—

$$\begin{array}{r}
 16.124 \\
 15.863 \\
 16.106 \\
 \hline
 \text{Mean, } 16.031, \pm .057.
 \end{array}$$

As the weighings were not reduced to a vacuum, this correction was afterwards applied by Clark,\* who showed that these syntheses really make  $O = 15.894$ ; or, in Berzelian terms, if  $O = 100$ ,  $H = 12.583$ . The value  $15.894, \pm .057$  we may therefore take as the true result of Dulong and Berzelius' experiments, a result curiously close to that reached in the latest and best researches.

In 1842 Dumas† published his elaborate investigation upon the composition of water. The first point was to get pure hydrogen. This gas, evolved from zinc and sulphuric acid, might contain oxides of nitrogen, sulphur dioxide, hydrosulphuric acid, and arsenic hydride. These impurities were removed in a series of wash bottles; the  $H_2S$  by a solution of lead nitrate, the  $H_3As$  by silver sulphate, and the others by caustic potash. Finally, the gas was dried by passing through sulphuric acid, or, in some of the experiments, over phosphorus pentoxide. The copper oxide was thoroughly dried, and the bulb containing it was weighed. By a current of dry hydrogen all the air was expelled from the apparatus, and then, for ten or twelve hours, the oxide of copper was heated to dull redness in a constant stream of the gas. The reduced copper was allowed to cool in an atmosphere of hydrogen. The weighings were made with the bulbs exhausted of air. The following table gives the results:

Column A contains the symbol of the drying substance; B gives the weight of the bulb and copper oxide; C, the weight of bulb and reduced copper; D, the weight of the vessel used for collecting the water; E, the same, plus the water; F, the weight of oxygen; G, the weight of water formed; H, the crude equivalent of H when  $O = 10,000$ ; I, the equivalent of H, corrected for the air contained in the sulphuric acid employed. This correction is not explained, and seems to be questionable.

\* Philosophical Magazine, 3d series, 20, 341.

† Compt. Rend., 14, 537.



In the sum total of these nineteen experiments, 840.161 grammes of oxygen form 945.439 grammes of water. This gives, in percentages, for the composition of water—oxygen, 88.864; hydrogen, 11.136. Hence the atomic weight of oxygen, calculated in mass, is 15.9608. In the following column the values are deduced from the individual data given under the headings F and G:

15.994
16.014
16.024
15.992
15.916
15.916
15.943
16.000
15.892
15.995
15.984
15.958
15.902
15.987
15.926
15.992
15.904
15.900
16.015

Mean, 15.9607, with a probable error of  $\pm .0070$ .

In calculating the above column several discrepancies were noted, probably due to misprints in the original memoir. On comparing columns B and C with F, or D and E with G, these anomalies chiefly appear. They were detected and carefully considered in the course of my own calculations; and, I believe, eliminated from the final result.

The investigation of Erdmann and Marchand\* followed closely after that of Dumas. The method of procedure was essentially that of the latter chemist, differing from it only in points of detail. The hydrogen used was prepared from zinc and sulphuric acid, and the zinc, which contained traces of carbon, was proved to be free from arsenic and sulphur. The copper oxide was made partly from copper turnings and partly by the ignition of the nitrate. The results obtained are given in two series, in one of which the weighings were not actually made in vacuo, but were, nevertheless, reduced to a vacuum standard. In the second series the copper oxide and copper were weighed in vacuo. The following table contains the corrected weights of water obtained and of the oxygen in it, with the value found for the atomic weight of oxygen in a third column. The weights are given in grammes.

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\* Journ. für Prakt. Chem., 1842, bd. 26, s. 461.

*First Series.*

<i>Wt. Water.</i>	<i>Wt. O.</i>	<i>At. Wt. O.</i>
62.980	55.950	15.917
95.612	84.924	15.891
94.523	84.007	15.977
35.401	31.461	15.970
		<u>15.939, <math>\pm .014</math></u>

*Second Series.*

<i>Wt. Water.</i>	<i>Wt. O.</i>	<i>At. Wt. O.</i>
41.664	37.034	15.996
44.089	39.195	16.018
53.232	47.321	16.011
55.636	49.460	16.017
		<u>16.010, <math>\pm .0036</math></u>

The effect of discussing these two series separately is somewhat startling. It gives to the four experiments in Erdmann and Marchand's second group a weight vastly greater than their other four and Dumas' nineteen taken together. For so great a superiority as this there is no adequate reason; and it is highly probable that it is due almost entirely to fortunate coincidences, rather than to greater accuracy of work. We will, therefore, treat Erdmann and Marchand's experiments as one series, giving all equal weight, the mean now becoming  $O = 15.975, \pm .0113$ . If we take the sum of the eight experiments, 483.137 grammes water and 429.352 grammes oxygen, and compute from these figures, then  $O = 15.966$ .

It would be easy to point out the sources of error in the foregoing sets of determinations, but it is hardly worth while to do so in detail. A few leading suggestions are enough for present purposes. First, there is an insignificant error due to the occlusion of hydrogen by metallic copper, rendering the apparent weight of the latter a trifle too high. Secondly, as shown by Dittmar and Henderson, hydrogen dried by passage through sulphuric acid becomes perceptibly contaminated with sulphur dioxide. In the third place, Morley\* has found that hydrogen prepared from zinc always contains carbon compounds not removable by absorption and washing. Erdmann and Marchand themselves note that their zinc contained traces of carbon. Finally, copper oxide, especially when prepared by the ignition of the nitrate, is very apt to contain gaseous impurities, and particularly occluded nitrogen.† Any or all of these sources of error may have vitiated the three investigations so far considered, but it would be useless to speculate as to the extent of their influence. They

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\*Amer. Chem. Journ., 12, 469. 1890.

† See Richards' work cited in the chapter on copper.



amply account, however, for the differences between the older and the later determinations of the constant under discussion.

Leaving out of account all measurements of the relative densities of hydrogen and oxygen, to be considered separately later, the next determination to be noted is that published by J. Thomsen in 1870.\* Unfortunately this chemist has not published the details of his work, but only the end results. Partly by the oxidation of hydrogen over heated copper oxide, and partly by its direct union with oxygen, Thomsen finds that at the latitude of Copenhagen, and at sea level, one litre of dry hydrogen at 0° and 760 mm. pressure will form .8041 gramme of water. According to Regnault, at this latitude, level, temperature, and pressure, a litre of hydrogen weighs .08954 gramme. From these data,  $O = 15.9605$ . It will be seen at once that Thomsen's work depends in great part upon that of Regnault, and is therefore subject to the corrections recently applied by Crafts and others to the latter. These corrections, which will be discussed further on, reduce the value of  $O$  from 15.9605 to 15.91. In order to combine this value with others, it is necessary to assign it weight arbitrarily, and as Thomsen made eight experiments, which are said to be concordant, it may be fair to rank his determination with that of Erdmann and Marchand, and to assume for it the same probable error. The value  $15.91, \pm .0113$  will therefore be taken as the outcome of Thomsen's research.

In 1887 Cooke and Richards published the results of their elaborate investigation.† These chemists weighed hydrogen, burned it over copper oxide, and weighed the water produced. The copper oxide was prepared from absolutely pure electrolytic copper, and the hydrogen was obtained from three distinct sources, as follows: First, from pure zinc and hydrochloric acid; second, by electrolysis, in a generator containing dilute hydrochloric acid and zinc-mercury amalgam; third, by the action of caustic potash solution upon sheet aluminum. The gas was dried and purified by passage through a system of tubes and towers containing potash, calcium chloride, glass beads drenched with sulphuric acid, and phosphorus pentoxide. No impurity could be discovered in it, and even nitrogen was sought for spectroscopically without being found.

The hydrogen was weighed in a glass globe holding nearly five litres and weighing 570.5 grammes, which was counterpoised by a second globe of exactly the same external volume. Before filling, the globe was exhausted to within 1 mm. of mercury and weighed. It was then filled with hydrogen and weighed again. The difference between the two weights gives the weight of hydrogen taken.

In burning, the hydrogen was swept from the globe into the combustion furnace by means of a stream of air which had previously been passed over hot reduced copper and hot cupric oxide, then through potash

\* *Berichte d. Deutsch. Chem. Gesell.*, 1870, s. 928.

† *Proc. Amer. Acad.*, 23, 149. *Am. Chem. Journ.*, 10, 81.

bulbs, and finally through a system of driers containing successively calcium chloride, sulphuric acid, and phosphorus pentoxide. The water formed by the combustion was collected in a condensing tube connected with a U tube containing phosphorus pentoxide. The latter was followed by a safety tube containing either calcium chloride or phosphorus pentoxide, added to the apparatus to prevent reflex diffusion. Full details as to the arrangement and construction of the apparatus are given. The final results appear in three series, representing the three sources from which the hydrogen was obtained. All weights are corrected to a vacuum.

*First Series.—Hydrogen from Zinc and Acid.*

<i>Wt. of H.</i>	<i>Wt. H<sub>2</sub>O.</i>	<i>At. Wt. O.</i>
.4233	3.8048	15.977
.4136	3.7094	15.937
.4213	3.7834	15.960
.4163	3.7345	15.941
.4131	3.7085	15.954
		Mean, 15.954, $\pm .0048$

*Second Series.—Electrolytic Hydrogen.*

<i>Wt. of H.</i>	<i>Wt. H<sub>2</sub>O.</i>	<i>At. Wt. O.</i>
.4112	3.6930	15.962
.4089	3.6709	15.955
.4261	3.8253	15.955
.4197	3.7651	15.942
.4144	3.7197	15.953
		Mean, 15.953, $\pm .0022$

*Third Series.—Hydrogen from Aluminum.*

<i>Wt. of H.</i>	<i>Wt. H<sub>2</sub>O.</i>	<i>At. Wt. O.</i>
.42205	3.7865	15.943
.4284	3.8436	15.944
.4205	3.7776	15.967
.43205	3.8748	15.937
.4153	3.7281	15.954
.4167	3.7435	15.967
		Mean, 15.952, $\pm .0035$
		Mean of all as one series, 15.953, $\pm .0020$

Shortly after the appearance of this paper by Cooke and Richards Lord Rayleigh pointed out the fact, already noted by Agamennone, that a glass globe when exhausted is sensibly condensed by the pressure of the surrounding atmosphere. This fact involves a correction to the foregoing data, due to a change in the tare of the globe used, and this correction was promptly determined and applied by the authors.\* By a

\* Proc. Amer. Acad., 23, 182. Am. Chem. Journ., 10, 191.

careful series of measurements they found that the correction amounted to an average increase of 1.98 milligrammes to the weight of hydrogen taken in each experiment. Hence O equals not 15.953, but 15.869, the probable error remaining unchanged. The final result of Cooke and Richards' investigation, therefore, is

$$O = 15.869, \pm .0020.$$

Keiser's determinations of the atomic weight of oxygen were published almost simultaneously with Cooke and Richards'. He burned hydrogen occluded by palladium, and weighed the water so formed. In a preliminary paper\* the following results are given:

<i>Wt. of H.</i>	<i>Wt. of H<sub>2</sub>O.</i>	<i>At. Wt. O.</i>
.65100	5.81777	15.873
.60517	5.41540	15.897
.33733	3.00655	15.822
		Mean, 15.864, $\pm .015$

Not long after the publication of the foregoing data Keiser's full paper appeared.† Palladium foil, warmed to a temperature of 250°, was saturated with hydrogen prepared from dilute sulphuric acid and zinc free from arsenic. From 100 to 140 grammes of palladium were taken, and it was first proved that the metal did not absorb other gases which might contaminate the hydrogen. Before charging, the foil was heated to bright redness in vacuo. After charging, the tube containing the palladium hydride was exhausted by means of a Geissler pump to remove any nitrogen which might have been present. In the preliminary investigation cited above, the latter precaution was neglected, which may account for the low results.

Between the palladium tube and the combustion tube a U tube was interposed, containing phosphorus pentoxide. This was to determine the amount of moisture in the hydrogen. The combustion tube was filled with granular copper oxide, prepared by reducing the commercial oxide in hydrogen, heating the metal so obtained to bright redness in a vacuum, and then reoxidizing with pure oxygen.

Upon warming the palladium tube, which was first carefully weighed, hydrogen was given off and allowed to pass into the combustion tube. When the greater part of it had been burned, the tube was cut off by means of a stopcock and allowed to cool. Meanwhile a stream of nitrogen was passed through the combustion tube, sweeping hydrogen before it. This was followed by a current of oxygen, reoxidizing the reduced copper; and the copper oxide was finally cooled in a stream of dry air. The water produced by the combustion was collected in a weighed bulb tube, followed by a weighed U tube containing phosphorus pentoxide.

\* *Berichte*, 20, 2323. 1887.

† *Amer. Chem. Journ.*, 10, 249. 1888.

A second phosphorus pentoxide tube served to prevent the sucking back of moisture from the external air. The loss in weight of the palladium tube, corrected by the gain in weight of the first phosphorus pentoxide, gave the weight of hydrogen taken. The gain in weight of the two collecting tubes gave the weight of water formed. All weights in the following table of results are reduced to a vacuum :

<i>Wt. of H.</i>	<i>Wt. H<sub>2</sub>O.</i>	<i>At. Wt. O.</i>
.34145	3.06338	15.943
.68394	6.14000	15.955
.65529	5.88200	15.952
.65295	5.86206	15.954
.66664	5.98116	15.944
.66647	5.98341	15.955
.57967	5.20493	15.958
.66254	5.94758	15.952
.87770	7.86775	15.950
.77215	6.93036	15.951

Mean, 15.9514,  $\pm .0011$ .

In sum, 6.55880 grammes of hydrogen gave 52.30383 of water, whence  $O = 15.9492$ .

In March, 1889, Lord Rayleigh\* published a few determinations of the atomic weight of oxygen obtained by still a new method. Pure hydrogen and pure oxygen were both weighed in glass globes. From these they passed into a mixing chamber, and thence into a eudiometer, where they were gradually exploded by a series of electric sparks. After explosion the residual gas remaining in the eudiometer was determined and measured. The results, given without weighings or explicit details, are as follows :

15.93
15.98
15.98
15.93
15.92

Mean, 15.948,  $\pm .009$

Correcting this result for shrinkage of the globes and consequent change of tare, it becomes  $O = 15.89, \pm .009$ .

In the same month that Lord Rayleigh's paper appeared, Noyes† published his first series of determinations. His plan was to pass hydrogen into an apparatus containing hot copper oxide, condensing the water formed in the same apparatus, and from the gain in weight of the latter getting the weight of the hydrogen absorbed. The apparatus devised for

\* Proc. Roy. Soc., 45, 425.

† Amer. Chem. Journ., 11, 155. 1889.

this purpose consisted essentially of a glass bulb of 30 to 50 cc. capacity, with a stopcock tube on one side and a sealed condensing tube on the other. In weighing, it was counterpoised by another apparatus of nearly the same volume but somewhat less weight, in order to obviate reductions to a vacuum. After filling the bulb with commercial copper oxide (90 to 150 grammes), the apparatus was heated in an airbath, exhausted by means of a Sprengel pump, cooled, and weighed. It was next replaced in the airbath, again heated, and connected with an apparatus delivering purified hydrogen. When a suitable amount of the latter had been admitted, the stopcock was closed, and the heating continued long enough to convert all gaseous hydrogen within it into water. The apparatus was then cooled and weighed, after which it was connected with a Sprengel pump, in order to extract the small quantity of nitrogen which was always present. The latter was pumped out into a eudiometer, where it was measured and examined. The gain in weight of the apparatus, less the weight of this very slight impurity, gave the weight of hydrogen oxidized.

The next step in the process consisted in heating the apparatus to expel water, and weighing again. After this, pure oxygen was admitted and the heating was resumed, so as to oxidize the traces of hydrogen which had been retained by the copper. Again the apparatus was cooled and weighed, and then reheated, when the water formed was received in a bulb filled with phosphorus pentoxide, and the gaseous contents were collected in a eudiometer. On cooling and weighing the apparatus, the loss of weight, less the weight of gases pumped out, gave the amount of water produced by the traces of residual hydrogen under consideration. This weight, added to the loss of weight when the original water was expelled, gives the weight of oxygen taken away from the copper oxide. Having thus the weight of hydrogen and the weight of oxygen, the atomic weight sought for follows. Six results are given, but as they are repeated, with corrections, in Noyes' second paper, they need not be considered now.

Noyes' methods were almost immediately criticised by Johnson,\* who suggested several sources of error. This chemist had already shown in an earlier paper† that copper reduced in hydrogen persistently retains traces of the latter, and also that when the reduction is effected below  $700^{\circ}$ , water is retained too. The possible presence of sulphur in the copper oxide was furthermore mentioned. Errors from these sources would tend to make the apparent atomic weight of oxygen too low.

In his second paper‡ Noyes replies to the foregoing criticisms, and shows that they carry no weight, at least so far as his work is concerned. He also describes a number of experiments in which oxides other than copper oxide were tried, but without distinct success, and he gives fuller

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\* Chem. News, 59, 272.

† Journ. Chem. Soc., May, 1879.

‡ Amer. Chem. Journ., 12, 441. 1890.

details as to manipulations and materials. His final results are in four series, as follows :

*First Series.—Hydrogen from Zinc and Hydrochloric Acid.*

<i>Wt. of H.</i>	<i>Wt. of O.</i>	<i>At. Wt. O.</i>
.9443	7.5000	15.885
.6744	5.3555	15.882
.7866	6.2569	15.909
.5521	4.3993	15.904
.4274	3.3997	15.909
.8265	6.5686	15.895

Mean, 15.8973,  $\pm .0032$ .

This series appeared in the earlier paper, but with an error which is here corrected.

*Second Series.—Electrolytic Hydrogen, Dried by Phosphorus Pentoxide.*

<i>Wt. of H.</i>	<i>Wt. of O.</i>	<i>At. Wt. O.</i>
.5044	4.0095	15.898
.6325	5.0385	15.932
.6349	5.0517	15.913
.5564	4.4175	15.879
.7335	5.8224	15.876
.6696	5.3181	15.885

Mean, 15.8971,  $\pm .0064$ .

*Third Series.—Electrolytic Hydrogen, Dried by Passage Through a Tube Packed with Sodium Wire.*

<i>Wt. of H.</i>	<i>Wt. of O.</i>	<i>At. Wt. O.</i>
.9323	7.4077	15.891
.9952	7.9045	15.885
.3268	2.5977	15.898
.7997	6.2798	15.884
.7762	6.1671	15.891
1.1221	8.9131	15.887

Mean, 15.8893,  $\pm .0014$

At the end of this series it was found that the hydrogen contained a trace of water, estimated to be equivalent to an excess of three milligrammes in the total hydrogen of the six experiments. Correcting for this, the mean becomes  $O = 15.890$ .

*Fourth Series.—Electrolytic Hydrogen, Dried over Freshly Sublimed Phosphorus Pentoxide.*

<i>Wt. of H.</i>	<i>Wt. of O.</i>	<i>At. Wt. O.</i>
1.0444	8.3017	15.898
.7704	6.1233	15.896
.8231	6.5421	15.896
.8872	7.0490	15.890
.9993	7.9403	15.892
1.1010	9.4595	15.885

Mean, 15.8929,  $\pm .0013$

The mean of all the twenty-four determinations, taken as one series, with the correction to the third series included, is  $O = 15.8966, \pm .0017$ . In sum, there were consumed 18.5983 grammes of hydrogen and 147.8145 of oxygen; whence  $O = 15.8955$ .

Dittmar and Henderson,\* who effected the synthesis of water over copper oxide by what was essentially the old method, begin their memoir with an exhaustive criticism of the work done by Dumas and by Erdmann and Marchand. They show, as I have already mentioned, that hydrogen dried by sulphuric acid becomes contaminated with sulphur dioxide, and also that a gas passed over calcium chloride may still retain as much as one milligramme of water per litre. Fused caustic potash they found to dry a gas quite completely.

In their first series of syntheses, Dittmar and Henderson generated their hydrogen from zinc and acid, sometimes hydrochloric and sometimes sulphuric, and dried it by passage, first through cotton wool, then through vitrioled pumice, then over red-hot metallic copper to remove oxygen. In later experiments it first traversed a column of fragments of caustic soda to remove antimony derived from the zinc. The oxide of copper used was prepared by heating chemically pure copper clippings in a muffle, and was practically free from sulphur. In weighing the several portions of apparatus it was tared with somewhat lighter similar pieces of as nearly as possible the same displacement. The results of this series of experiments, which are vitiated by the presence, unsuspected at first, of sulphur dioxide in the hydrogen, are stated in values of H when  $O = 16$ , but in the following table have been recalculated to the usual unit:

<i>Wt. of Water.</i>	<i>Wt. of O.</i>	<i>At. Wt. O.</i>
4.7980	4.26195	15.901
7.55025	6.71315	16.039
6.2372	5.53935	15.875
11.29325	10.03585	15.963
11.6728	10.3715	15.940
11.8433	10.5256	15.976
11.7317	10.4243	15.947
19.2404	17.0926	15.916
20.83435	18.5234	16.031
17.40235	15.4598	15.917
19.2631	17.11485	15.934

Mean,  $15.949, \pm .0103$ .

Reducing to a vacuum, this becomes 15.843, while a correction for the sulphur dioxide estimated to be present in the hydrogen brings the value

\* Proc. Roy. Soc. Glasgow, 22, 33. Communicated Dec. 17, 1890.

up again to 15.865. Still another correction is suggested, namely, that as the reduced copper in the combustion tube, before weighing, was exposed to a long-continued current of dry air, it may have taken up traces of oxygen chemically, thereby increasing its weight. As this correction, however, is quantitatively uncertain, it may be neglected here, and the result of this series will be taken as  $O = 15.865, \pm .0103$ . Its weight, relatively to some other series of experiments, is evidently small.

In their second and final series Dittmar and Henderson dried their hydrogen, after deoxidation by red-hot copper, over caustic potash and subsequently phosphorus pentoxide. The copper oxide and copper of the combustion tube were both weighed in vacuo. The results were as follows, vacuum weights being given :

<i>Wt. Water.</i>	<i>Wt. O.</i>	<i>At. Wt. O.</i>
19.2057	17.0530	15.843
19.5211	17.3342	[15.853]
19.4672	17.2882	15.868
22.9272	20.3540	15.820
23.0080	20.4421	[15.934]
23.4951	20.8639	15.859
23.5612	20.9226	[15.859]
23.7542	21.0957	15.870
23.6568	21.8994	15.884
23.6179	21.8593	15.848
24.6021	21.8499	15.878
24.3047	21.5788	15.832
23.6172	20.9709	15.849

Mean, 15.861,  $\pm .0052$ .

The authors reject the three bracketed determinations, because of irregularities in the course of the experiments. The mean of the ten remaining determinations is 15.855,  $\pm .0044$ . Both means, however, have to be corrected for the minute trace of hydrogen occluded by the reduced copper. This correction, experimentally measured, amounts to  $+.006$ . Hence the mean of all the experiments in the series becomes 15.867,  $\pm .0052$ , and of the ten accepted experiments, 15.861,  $\pm .0044$ . The authors themselves select out seven experiments, giving a corrected mean of 15.866, which they regard as the best value. Taking all their evidence, their two series combine thus :

First series.....	15.865, $\pm .0103$
Second series.....	15.867, $\pm .0052$
General mean.....	15.8667, $\pm .0046$

Leduc,\* who also effected the synthesis of water over copper oxide,

\* Compt. Rend., 115, 41. 1892.



following Dumas' method with slight modifications, gives the results of only two experiments, as follows:

<i>Wt. Water.</i>	<i>Wt. O.</i>	<i>At. Wt. O.</i>
22.1632	19.6844	15.882
19.7403	17.5323	15.880
		<hr/> Mean, 15.881

These experiments we may arbitrarily assign equal weight with two in Dittmar and Henderson's later series, when the result becomes 15.881,  $\pm .0132$ , the value to be accepted. Ledue states that his copper oxide, which was reduced at as low a temperature as possible, was prepared by heating clippings of electrolytic copper in a stream of oxygen.

To E. W. Morley \* we owe the first complete quantitative syntheses of water, in which both gases were weighed separately, and afterwards in combination. The hydrogen was weighed in palladium, as was done by Keiser, and the oxygen was weighed in compensated globes, after the manner of Regnault. The globes were contained in an artificial "cave," to protect them from moisture and from changes of temperature; being so arranged that they could be weighed by the method of reversals without opening either the "cave" or the balance case. For each weighing of hydrogen about 600 grammes of palladium were employed. After weighing, the gases were burnt by means of electric sparks in a suitable apparatus, from which the unburned residue could be withdrawn for examination. Finally, the apparatus containing the water produced was closed by fusion and also weighed. Rubber joints were avoided in the construction of the apparatus, and the connections were continuous throughout. The weights are as follows:

<i>H taken</i>	<i>O taken.</i>	<i>H<sub>2</sub>O formed.</i>
3.2645	25.9176	29.1788
3.2559	25.8531	29.1052
3.8193	30.3210	34.1389
3.8450	30.5294	Lost
3.8382	30.4700	34.3151
3.8523	30.5818	34.4327
3.8298	30.4013	34.2284
3.8286	30.3966	34.2261
3.8225	30.3497	34.1742
3.8220	30.3479	34.1743
3.7637	29.8865	33.6540
3.8211	30.3429	34.1559

\* "On the Density of Oxygen and Hydrogen, and on the Ratio of their Atomic Weights," by Edward W. Morley. Smithsonian Contributions to Knowledge, 1895, 4to, xi + 117 pp., 40 cuts. Abstract in Am. Chem. Journ., 17, 267 (gravimetric), and Ztschr. Phys. Chem., 17, 87 (gaseous densities); also note in Am. Chem. Journ., 17, 396. Preliminary notice in Proc. Amer. Association, 1891, p. 185.

Hence we have—

<i>H: O Ratio</i>	<i>H: H<sub>2</sub>O Ratio.</i>
15.878	17.877
15.881	17.878
15.878	17.873
15.880	.....
15.877	17.881
15.877	17.876
15.877	17.875
15.878	17.879
15.879	17.881
15.881	17.883
15.881	17.883
15.882	17.878
<hr/> Mean, 15.8792, $\pm$ .00032	<hr/> Mean, 17.8785, $\pm$ .00066

Combined, these data give:

From ratio $H_2: O$ . . . . .	$O = 15.8792, \pm .00032$
“ “ $H_2: H_2O$ . . . . .	$O = 15.8785, \pm .00066$
General mean . . . . .	$O = 15.8790, \pm .00028$

For details, Morley's full paper must be consulted. No abstract can do justice to the remarkable work therein recorded.

Two other series of determinations, by Julius Thomsen, remain to be noticed. In the earlier paper\* he determined the ratio between HCl and  $NH_3$ , and thence, using Stas' values for Cl and N, fixed by reference to  $O = 16$ , computed the ratio  $H: O$ . This method was so indirect as to be of little importance, and gave for the atomic weight of oxygen approximately the round number 16. I shall use the data farther on in calculating the atomic weight of nitrogen. The paper has been sufficiently criticised by Meyer and Seubert,† who have discussed its sources of error.

In Thomsen's later paper‡ a method of determination is described which is, like the preceding, quite novel, but more direct. First, aluminum, in weighed quantities, was dissolved in caustic potash solution. In one set of experiments the apparatus was so constructed that the hydrogen evolved was dried and then expelled. The loss of weight of the apparatus gave the weight of the hydrogen so liberated. In the second set of experiments the hydrogen passed into a combustion chamber in which it was burned with oxygen, the water being retained. The increase in weight of this apparatus gave the weight of oxygen so taken up. The two series, reduced to the standard of a unit weight of aluminum, gave the ratio between oxygen and hydrogen.

\* Zeitsch. Physikal. Chem., 13, 398. 1894.

† Ber., 27, 2770.

‡ Zeitsch. Anorg. Chem., 11, 14. 1895.

The results of the two series, reduced to a vacuum and stated as ratios, are as follows :

<i>First.</i>	<i>Second.</i>
$\frac{\text{Weight of H.}}{\text{Weight of Al}}$	$\frac{\text{Weight of O}}{\text{Weight of Al}}$
0.11180	0.88788
0.11175	0.88799
0.11194	0.88774
0.11205	0.88779
0.11189	0.88785
0.11200	0.88789
0.11194	0.88798
0.11175	0.88787
0.11190	0.88773
0.11182	0.88798
0.11204	0.88785
0.11202	—————
0.11204	0.88787, $\pm 0.000018$
0.11179	
0.11178	
0.11202	
0.11188	
0.11186	
0.11185	
0.11190	
0.11187	
—————	
0.11190, $\pm 0.000015$	

Dividing the mean of the second column by the mean of the first, we have for the equivalent of oxygen :

$$\frac{0.88787, \pm 0.000018}{0.11190, \pm 0.000015} = 7.9345, \pm 0.0011$$

Hence  $O = 15.8690, \pm 0.0022$ .

The details of the investigation are somewhat complicated, and involve various corrections which need not be considered here. The result as stated includes all corrections and is evidently good. The ratios, however, cannot be reversed and used for measuring the atomic weight of aluminum, because the metal employed was not absolutely pure.

We have now before us, representing syntheses of water, thirteen series, as follows :

Dulong and Berzelius.....	O = 15.894, $\pm .057$
Dumas.....	15.9607, $\pm .0070$
Erdmann and Marchand.....	15.975, $\pm .0113$
Thomsen, 1870.....	15.91, $\pm .0113$
Cooke and Richards.....	15.869, $\pm .0020$
Keiser, 1887.....	15.864, $\pm .015$
“ 1888.....	15.9514, $\pm .0011$

Rayleigh.....	15.89, $\pm .009$
Noyes.....	15.8966, $\pm .0017$
Dittmar and Henderson.....	15.8667, $\pm .0046$
Leduc.. ..	15.881, $\pm .0132$
Morley.....	15.8790, $\pm .00028$
Thomsen, 1895.....	15.8690, $\pm .0022$
<hr/>	
General mean.....	O = 15.8837, $\pm .00026$
Rejecting Keiser.....	15.8796, $\pm .00027$

If we reject all except the determinations of Cooke and Richards, Rayleigh, Noyes, Dittmar and Henderson, Leduc, Thomsen, and Morley, the general mean of these becomes 15.8794,  $\pm .00027$ . From this it is evident that Keiser's determinations alone, among the higher values for O, carry any appreciable weight; and it also seems clear that the rounded-off number, O = 15.88,  $\pm .0003$ , cannot be very far from the truth; at least so far as the synthetic evidence goes.

In discussing the relative densities of oxygen and hydrogen gases we need consider only the more modern determinations, beginning with those of Dumas and Boussingault. As the older work has some historical value, I may in passing just cite its results. For the density of hydrogen we have .0769, Lavoisier; .0693, Thomson; .092, Cavendish; .0732, Biot and Arago; .0688, Dulong and Berzelius. For oxygen there are the following determinations: 1.087, Foureroy, Vauquelin, and Séguin; 1.103, Kirwan; 1.128, Davy; 1.088, Allen and Pepys; 1.1036, Biot and Arago; 1.1117, Thomson; 1.1056, De Saussure; 1.1026, Dulong and Berzelius; 1.106, Buff; 1.1052, Wrede.\*

In 1841 Dumas and Boussingault † published their determinations of gaseous densities. For hydrogen they obtained values ranging from .0691 to .0695; but beyond this mere statement they give no details. For oxygen three determinations were made, with the following results:

1.1055
1.1058
1.1057
<hr/>
Mean, 1.10567, $\pm .00006$

If we take the two extreme values given above for hydrogen, and regard them as the entire series, they give us a mean of .0693,  $\pm .00013$ . This mean hydrogen value, combined with the mean for oxygen, gives for the latter, when H = 1, the density ratio 15.9538,  $\pm .031$ .

Regnault's researches, published four years later, ‡ were much more

\* For Wrede's work, see Berzelius' Jahresbericht for 1843. For Dulong and Berzelius, see the paper already cited. All the other determinations are taken from Gmelin's Handbook, Cavendish edition, v. 1, p. 279.

† Compt. Rend., 12, 1005. Compare also with Dumas, Compt. Rend., 14, 537.

‡ Compt. Rend., 20, 975.

elaborately executed. Indeed, they have long stood among the classics of physical science, and it is only recently that they have been supplanted by other measurements.

For hydrogen three determinations of density gave the following results:

$$\begin{array}{r} .06923 \\ .06932 \\ .06924 \\ \hline \text{Mean, } .069263, \pm .000019 \end{array}$$

For oxygen four determinations were made, but in the first one the gas was contaminated by traces of hydrogen, and the value obtained, 1.10525, was, therefore, rejected by Regnault as too low. The other three are as follows:

$$\begin{array}{r} 1.10561 \\ 1.10564 \\ 1.10565 \\ \hline \text{Mean, } 1.105633, \pm .000008 \end{array}$$

Now, combining the hydrogen and oxygen series, we have the ratio H : O : : 1 : 15.9628,  $\pm .0044$ . According to Le Conte,\* Regnault's reductions contain slight numerical errors, which, corrected, give for the density of oxygen, 1.105612, and for hydrogen, .069269. Ratio, 1 : 15.9611.

A much weightier correction to Regnault's data has already been indicated in the discussion of Cooke and Richards' work. He assumed that the globes in which the gases were weighed underwent no changes of volume, but Agamennone,† and after him, but independently,‡ Lord Rayleigh showed that an exhausted vessel was perceptibly compressed by atmospheric pressure. Hence its volume when empty was less than its volume when filled with gas. Crafts, having access to Regnault's original apparatus, has determined the magnitude of the correction indicated.§ Unfortunately, the globe actually used by Regnault had been destroyed, but another globe of the same lot was available. With this the amount of shrinkage during exhaustion was measured, and Regnault's densities were thereby changed to 1.10562 for oxygen, and .06949 for hydrogen. Corrected ratio, 1 : 15.9105. Doubtless Dumas and Boussingault's data are subject to a similar correction, and if we assume that it is proportionally the same in amount, the ratio derived from their experiments becomes 1 : 15.9015.

In the same paper, that which contained the discovery of this correction, Lord Rayleigh gives a short series of measurements of his own.

\* Private communication. See also Phil. Mag. (4), 27, 29, 1864, and Smithsonian Report, 1878, p. 428.

† Atti Rendiconti Acad. Lincei, 1855.

‡ Proc. Roy. Soc., 43, 356. Feb., 1888.

§ Compt. Rend., 106, 1662.

His hydrogen was prepared from zinc and sulphuric acid, and was purified by passage over liquid potash, then through powdered mercuric chloride, and then through pulverized solid potash. It was dried by means of phosphorus pentoxide. His oxygen was derived partly from potassium chlorate, and partly from the mixed chlorates of sodium and potassium. Equal volumes of the two gases weighed as follows :

<i>H.</i>	<i>O.</i>
.15811	2.5186, $\pm .00061$ *
.15807	
.15798	
.15792	
Mean, .15802, $\pm .000029$ .	

Corrected for shrinkage of the exhausted globe these become—H, 0.15860; O, 2.5192. Hence the ratio 1 : 15.884,  $\pm .0048$ .

In 1892 Rayleigh published a much more elaborate determination of this ratio.† The gases were prepared electrolytically from caustic potash, and dried by means of solid potash and phosphorus pentoxide. The hydrogen was previously passed over hot copper. The experiments, stated like the previous series, are in five groups; two for oxygen and three for hydrogen; but for present purposes the similar sets may be regarded as equal in weight, and so discussable together. The weights of equal volumes are as follows :

	<i>H.</i>		<i>O.</i>	
First set	.15807	}	2.5182	First set.
	.15816		2.5173	
	.15811		2.5172	
	.15803		2.5193	
	.15801		2.5174	
Mean, .15808	.15809		2.5177	Mean, 2.51785.
Second set	.15800	}	2.5183	
	.15820		2.5168	
	.15792		2.5172	
	.15788		2.5181	
	.15783		2.5156	
Mean, .15797	.15807			Mean, 2.5176, $\pm .00019$ .
Third set	.15801	}		
	.15817			
	.15790			
	.15810			
	.15798			
Mean, .15804	.15802			
	.15807			
	Mean, .15804, $\pm .000019$ .			

\* Arbitrarily assigned the probable error of a single experiment in Rayleigh's paper of 1892.

† Proc. Roy. Soc., 50, 448, Feb. 18, 1892.

These weights with various corrections relative to temperatures and pressures, and also for the compression of the exhausted globe, ultimately become for H, .158531; and for O, 2.51777. Hence the ratio 1 : 15.882,  $\pm$  .0023. For details relative to corrections the original memoir should be consulted.

In his paper "On a new method of determining gas densities,"\* Cooke gives three measurements for hydrogen, referred to air as unity. They are:

$$\begin{array}{r} .06957 \\ .06951 \\ .06966 \\ \hline \text{Mean, } .06958, \pm .000029 \end{array}$$

Combining this with Regnault's density for oxygen, as corrected by Crafts, 1.10562,  $\pm$  .000008, we get the ratio H : O :: 1 : 15.890,  $\pm$  .0067.

Leduc, working by Regnault's method, somewhat modified, and correcting for shrinkage of exhausted globes, gives the following densities: †

<i>H.</i>	<i>O.</i>
.06947	1.10501
.06949	1.10516
.06947	
<u>          </u>	
Mean, .06948, $\pm$ .00006745	

The two oxygen measurements are the extremes of three, the mean being 1.10506,  $\pm$  .0000337. Hence the ratio 1 : 15.905,  $\pm$  .0154.

The first two hydrogen determinations were made with gas produced by the electrolysis of caustic potash, while the third sample was derived from zinc and sulphuric acid. The oxygen was electrolytic. Both gases were passed over red-hot platinum sponge, and dried by phosphorus pentoxide.

Much more elaborate determinations of the two gaseous densities are those made by Morley. ‡ For oxygen he gives three series of data; two with oxygen from potassium chlorate, and one with gas partly from the same source and partly electrolytic. In the first series, temperature and pressure were measured with a mercurial thermometer and a manometer. In the second series they were not determined for each experiment, but were fixed by comparison with a standard volume of hydrogen by means of a differential manometer. In the third series the gas was kept at the temperature of melting ice, and the manometer

\* Proc. Amer. Acad., 24, 202. 1889. Also Am. Chem. Journ., 11, 509.

† Compt. Rend., 113, 186. 1891.

‡ Paper already cited, under the gravimetric portion of this chapter.

alone was read. The results for the weight in grammes, at latitude  $45^\circ$ , of one litre of oxygen are as follows :

<i>First Series.</i>	<i>Second Series.</i>	<i>Third Series.</i>
1.42864	1.42952	1.42920
1.42849	1.42900	1.42860
1.42838	1.42863	1.42906
1.42900	1.42853	1.42957
1.42907	1.42858	1.42910
1.42887	1.42873	1.42930
1.42871	1.42913	1.42945
1.42872	1.42905	1.42932
1.42883	1.42896	1.42908
-----	1.42880	1.42910
Mean, 1.42875, $\pm .000051$	1.42874	1.42951
Corrected,* 1.42879, $\pm .000051$	1.42878	1.42933
	1.42872	1.42905
	1.42859	1.42914
	1.42851	1.42849
	-----	1.42894
	Mean, 1.42882, $\pm .000048$	1.42886
	Corrected, 1.42887, $\pm .000048$	-----
		Mean, 1.42912, $\pm .000048$
		Corrected, 1.42917, $\pm .000048$

General mean of all three series,  $1.42896, \pm .000028$ .

Morley himself, for experimental reasons, prefers the last series, and gives it double weight, getting a mean density of 1.42900. The difference between this mean and that given above is insignificant with reference to the atomic weight problem.

In the case of hydrogen, Morley's determinations fall into two groups, but in both the gas was prepared by the electrolysis of pure dilute sulphuric acid, and was most elaborately purified. In the first group there are two series of measurements. Of these, the first involved the reading of temperature and pressure by means of a mercurial thermometer and mano-barometer. In the second series, the gas was delivered into the weighing globes after occlusion in palladium; it was then kept at the temperature of melting ice, and only the syphon barometer was read. In this group the hydrogen was possibly contaminated with mercurial vapor, and the results are discarded by Morley in his final summing up. For present purposes, however, it is unnecessary to reject them, for they have confirmatory value, and do not appreciably affect the final mean. The weight of one litre of hydrogen at  $45^\circ$  latitude, as found in these two sets of determinations, is as follows :

\* Correction applied by Morley to all his series, for a slight error,  $\frac{1}{300000}$ , in the length of his standard metre bar.



<i>First Series.</i>	<i>Second Series.</i>
.089904	.089977
.089936	.089894
.089945	.089987
.089993	.089948
.089974	.089951
.089941	.089960
.089979	.090018
.089936	.089909
.089904	.089953
.089863	.089974
.089878	.089922
.089920	.090093
.089990	.090007
.089926	.089899
.089928	.089974
-----	.089900
Mean, .089934, $\pm$ .000007	.089869
Corrected, .089938, $\pm$ .000007	.090144
	.089984
	-----
	Mean, .089967, $\pm$ .000011
	Corrected, .089970, $\pm$ .000011

In the second group of experiments, the hydrogen was weighed in palladium before transfer to the calibrated globe; and in weighing, the palladium tube was tared by a similar apparatus of nearly equal volume and weight. After transfer, which was effected without the intervention of stopcocks, the volume and pressure of the gas were taken at the temperature of melting ice. A preliminary set of measurements was made, followed by three regular series; of these, the first and second were with the same apparatus, and are different only in point of time, a vacation falling between them. The last series was with a different apparatus. The data are as follows, with the means as usual:

<i>Preliminary.</i>	<i>Third Series.</i>	<i>Fourth Series.</i>	<i>Fifth Series.</i>
.089946	.089874	.089972	.089861
.089915	.089891	.089877	.089877
.089881	.089886	.089867	.089870
.089901	.089866	.089916	.089867
.089945	.089911	.089770	.089839
-----	.089856	.089846	.089874
Mean, .089918,	.089912	-----	.089864
$\pm$ .0000271	.089872	Mean, .089875,	.089883
Corrected, .089921	-----	$\pm$ .0000187	.089830
	Mean, .089883,	Corrected, .089880	.089877
	$\pm$ .000049		.089851
	Corrected, .089886		-----
			Mean, .089863,
			$\pm$ .0000034
			Corrected, .089866

Now, rejecting nothing, we may combine all the series into a general mean, giving the weight of one litre of hydrogen as follows :

First series.....	.089938, $\pm$ .000007
Second series .. . . .	.089970, $\pm$ .000011
Preliminary series, second method.....	.089921, $\pm$ .0000271
Third series.....	.089886, $\pm$ .0000049
Fourth “ .....	.089880, $\pm$ .0000187
Fifth “ .....	.089866, $\pm$ .0000034
<hr/>	
General mean.....	.089897, $\pm$ .0000025
Rejecting the first three.....	.089872, $\pm$ .0000028

This last mean value for hydrogen will be used in succeeding chapters of this work for reducing volumes of the gas to weights. Combining the general mean of all with the value found for the weight of a litre of oxygen, 1.42896,  $\pm$  .000028, we get for the ratio H : O,

$$\text{O} = 15.8955, \pm .0005$$

If we take only the second mean for H, excluding the first three series, we have—

$$\text{O} = 15.9001, \pm .0005$$

This value is undoubtedly nearest the truth, and is preferable to all other determinations of this ratio. Its probable error, however, is given too low ; for some of the oxygen weighings involved reductions for temperature and pressure. These reductions involve, again, the coefficient of expansion of the gas, and its probable error should be included. Since, however, that factor has been disregarded elsewhere, it would be an over-refinement of calculation to include it here.

In a memoir of this kind it is impossible to do full justice to so elaborate an investigation as that of Morley. The details are so numerous, the corrections so thorough, the methods for overcoming difficulties so ingenious, that many pages would be needed in order to present anything like a satisfactory abstract. Hardly more than the actual results can be cited here ; for all else the original memoir must be consulted.

Still more recently, by a novel method, J. Thomsen has measured the two densities in question.\* In his gravimetric research, already cited, he ascertained the weights of hydrogen and of oxygen equivalent to a unit weight of aluminum. In his later paper he describes a method of measuring the corresponding volumes of both gases during the same reactions. Then, having already the weights of the gases, the volume-weight ratio, or density, is in each case easily computable. From 1.0171 to 2.3932 grammes of aluminum were used in each experiment. Omitting details, the volume of hydrogen in litres, equivalent to one gramme of the metal, is as follows :

---

\* Zeitschr. Anorg. Chem., 12, 4. 1896.

1.24297
1.24303
1.24286
1.24271
1.24283
1.24260
1.24314
1.24294

Mean, 1.24289,  $\pm .00004$

The weight of hydrogen evolved from one gramme of aluminum was found in Thomsen's gravimetric research to be 0.11190,  $\pm .000015$ . Hence the weight of one litre at 0°, 760 mm., and 10.6 meters above sea level at Copenhagen is :

$$.090032, \pm .000012;$$

or at sea level in latitude 45°,

$$.089947, \pm .000012 \text{ gramme.}$$

The data for oxygen are given in somewhat different form, namely, for the volume of one gramme of the gas at 0°, 760, and at Copenhagen. The values are, in litres :

.69902
.69923
.69912
.69917
.69903
.69900
.69901
.69921
.69901
.69922

Mean, .69910,  $\pm .00002$

At sea level in latitude 45°, .69976,  $\pm .00002$

Hence one litre weighs 1.42906,  $\pm .00004$  grammes.

Dividing this by the weight found for hydrogen, 0.089947,  $\pm .000012$  we have for the ratio H : O,

$$15.8878, \pm .0022.$$

The density ratios, H : O, now combine as follows :

Dumas and Boussingault, corrected.....	15.9015, $\pm .031$
Regnault, corrected.....	15.9105, $\pm .0044$
Rayleigh, 1888.....	15.884, $\pm .0048$
“ 1892.....	15.882, $\pm .0023$
Cooke.....	15.890, $\pm .0067$
Leduc.....	15.905, $\pm .0154$
Morley, including all the data.....	15.8955, $\pm .0005$
Thomsen.....	15.8878, $\pm .0022$
General mean.....	15.8948, $\pm .00048$

If we reject all of Morley's data for the density of hydrogen except his third, fourth, and fifth series, the mean becomes

$$O = 15.8991, \pm .00048.$$

In either case Morley's data vastly outweigh all others.'

If oxygen and hydrogen were perfect gases, uniting by volume to form water exactly in the ratio of one to two, then the density of the first in terms of the second would also express its atomic weight. But in fact, the two gases vary from Boyle's law in opposite directions, and the true composition of water by volume diverges from the theoretical ratio to a measurable extent. Hence, in order to deduce the atomic weight of oxygen from its density, a small correction must be applied to the latter, dependent upon the amount of this divergence. Until recently, our knowledge of the volumetric composition of water rested entirely upon the determinations made by Humboldt and Gay-Lussac\* early in this century, which gave a ratio between H and O of a little less than 2:1, but their data need no farther consideration here.

In 1887 Scott † published his first series of experiments, 21 in number, finding as the most probable result a value for the ratio of 1.994:1. In March, 1888, ‡ he gave four more determinations, ranging from 1.9962 to 1.998:1; and later in the same year § another four, with values from 1.995 to 2.001. In 1893, || however, by the use of improved apparatus, he was able to show that his previous work was vitiated by errors, and to give a series of measurements of far greater value. Of these, twelve were especially good, being made with hydrogen from palladium hydride, and with oxygen from silver oxide. In mean the value found is 2.00245,  $\pm$  .00007, with a range from 2.0017 to 2.0030.

In 1891 an elaborate paper by Morley ¶ appeared, in which twenty concordant determinations of the volumetric ratio gave a mean value of 2.00023,  $\pm$  .000015. These measurements were made in eudiometer tubes, and were afterwards practically discarded by the author. In his later and larger paper, \*\* however, he redetermined the ratio from the density of the mixed electrolytic gases, and found it to be, after applying all corrections, 2.00274. The probable error, roughly estimated, is .00005. Morley also reduces Scott's determinations, which were made at the temperature of the laboratory, to 0°, when the value becomes 2.00285. The mean value of both series may therefore be put at 2.0028,  $\pm$  .00004, with sufficient accuracy for present purposes. Ledue's †† single determination,

\* Journ. de Phys., 60, 129.

† Proc. Roy. Soc., 42, 396.

‡ Nature, 37, 439.

§ British Assoc. Report, 1888, 631.

|| Proc. Roy. Soc., 53, 130. In full in Philosophical Transactions, 184, 543. 1893.

¶ Amer. Journ. Sci. (3), 46, 220, and 276.

\*\* Already cited with reference to syntheses of water.

†† Compt. Rend., 115, 311. 1892.

based upon the density of the mixed gases obtained by the electrolysis of water, gave 2.0037; but Morley shows that some corrections were neglected. This determination, therefore, may be left out of account.

Now, including all data, we have a mean value for the density ratio:

$$(A.) \quad \text{H : O :: 1 : 15.8948, } \pm .00048;$$

or, omitting Morley's rejected series,

$$(B.) \quad \text{H : O :: 1 : 15.8991, } \pm .00048.$$

Correcting these by the volume ratio, 2.0028,  $\pm .00004$ , the final result for the atomic weight of oxygen as determined by gaseous densities becomes:

$$\begin{array}{l} \text{From A. .... O = 15.8726, } \pm .00058 \\ \text{From B. .... O = 15.8769, } \pm .00058 \end{array}$$

Combining these with the result obtained from the syntheses of water, rejecting nothing, we have—

$$\begin{array}{l} \text{By synthesis of water. .... O = 15.8837, } \pm .00026 \\ \text{By gaseous densities. .... O = 15.8726, } \pm .00058 \\ \hline \text{General mean. .... O = 15.8821, } \pm .00024 \end{array}$$

If we reject Keiser's work under the first heading, and omit Morley's defective hydrogen series under the second, we get—

$$\begin{array}{l} \text{By synthesis of water .... O = 15.8796, } \pm .00027 \\ \text{By gaseous densities. .... O = 15.8769, } \pm .00058 \\ \hline \text{General mean. .... O = 15.8794, } \pm .00025 \end{array}$$

Morley, discussing his own data, gets a final value of  $\text{O} = 15.8790, \pm .00026$ , a result sensibly identical with the second of the means given above. These results cannot be far from the truth; and accordingly, rounding off the last decimals, the value

$$\text{O} = 15.879, \pm .0003,$$

will be used in computation throughout this work.

NOTE.—A useful "short bibliography" upon the composition of water, by T. C. Warrington, may be found in the Chemical News, vol. 73, pp. 137, 145, 156, 170, and 184.

## SILVER, POTASSIUM, SODIUM, CHLORINE, BROMINE, AND IODINE.

The atomic weights of these six elements depend upon each other to so great an extent that they can hardly be considered independently. Indeed, chlorine, potassium, and silver have always been mutually determined. From the ratio between silver and chlorine, the ratio between silver and potassium chloride, and the composition of potassium chlorate, these three atomic weights were first accurately fixed. Similar ratios, more recently worked out by Stas and others, have rendered it desirable to include bromine, iodine, and sodium in the same general discussion.

Several methods of determination will be left altogether out of account. For example, in 1842 Marignac\* sought to fix the atomic weight of chlorine by estimating the quantity of water formed when hydrochloric acid gas is passed over heated oxide of copper. His results were wholly inaccurate, and need no further mention here. A little later Laurent† redetermined the same constant from the analysis of a chlorinated derivative of naphthalene. This method did not admit of extreme accuracy, and it presupposed a knowledge of the atomic weight of carbon; hence it may be properly disregarded. Maumené's‡ analyses of the oxalate and acetate of silver gave good results for the atomic weight of that metal; but they also depend for their value upon our knowledge of carbon, and will, therefore, be discussed farther on with reference to that element. Hardin's§ work also, relating to the nitrate, acetate, and benzoate of silver, will be found in the chapters upon nitrogen and carbon.

Let us now consider the ratios upon which we must rely for ascertaining the atomic weights of the six elements in question. After we have properly arranged our data we may then discuss their meaning. First in order we may conveniently take up the percentage of potassium chloride obtainable from the chlorate.

The first reliable series of experiments to determine this percentage was made by Berzelius.|| All the earlier estimations were vitiated by the fact that when potassium chlorate is ignited under ordinary circumstances a little solid material is mechanically carried away with the oxygen gas. Minute portions of the substance may even be actually volatilized. These sources of loss were avoided by Berzelius, who devised means for collecting and weighing this trace of potassium chloride.

\* Compt. Rend., 14, 570. Also, Journ. f. Prakt. Chem., 26, 304.

† Compt. Rend., 14, 456. Journ. f. Prakt. Chem., 26, 307.

‡ Ann. d. Chim. et d. Phys. (3), 18, 41. 1846.

§ Journ. Amer. Chem. Soc. 18, 990. 1896.

|| Poggend. Annalen, 8, 1. 1826.

All the successors of Berzelius in this work have benefited by his example, although for the methods by which loss has been prevented we must refer to the original papers of the several investigators. In short, then, Berzelius ignited potassium chlorate, and determined the percentage of chloride which remained. Four experiments gave the following results :

60.854
60.850
60.850
60.851
<hr/>
Mean, 60.851, $\pm .0006$

The next series was made by Penny,\* in England, who worked after a somewhat different method. He treated potassium chlorate with strong hydrochloric acid in a weighed flask, evaporated to dryness over a sand bath, and then found the weight of the chloride thus obtained. His results are as follows, in six trials :

60.825
60.822
60.815
60.820
60.823
60.830
<hr/>
Mean, 60.8225, $\pm .0014$

In 1842 Pelouze† made three estimations by the ignition of the chlorate, with these results :

60.843
60.857
60.830
<hr/>
Mean, 60.843, $\pm .0053$

Marignac, in 1842,‡ worked with several different recrystallizations of the commercial chlorate. He ignited the salt, with the usual precautions for collecting the material carried off mechanically, and also examined the gas which was evolved. He found that the oxygen from 50 grammes of chlorate contained chlorine enough to form .003 gramme of silver chloride. Here are the percentages found by Marignac :

In chlorate once crystallized . . . . .	60.845
In chlorate once crystallized . . . . .	60.835
In chlorate twice crystallized . . . . .	60.833
In chlorate twice crystallized . . . . .	60.844
In chlorate three times crystallized . . . . .	60.839
In chlorate four times crystallized . . . . .	60.839
<hr/>	
Mean, 60.8392, $\pm .0013$	

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\* Phil. Transactions, 1839, p. 20.

† Compt. Rend., 15, 959.

‡ Ann. d. Chem. u. Pharm., 44, 18.

In the same paper Marignac describes a similar series of experiments made upon potassium perchlorate,  $\text{KClO}_4$ . In three experiments it was found that the salt was not quite free from chlorate, and in three more it contained traces of iron. A single determination upon very pure material gave 46.187 per cent. of oxygen and 53.813 of residue.

In 1845 two series of experiments were published by Gerhardt.\* The first, made in the usual way, gave these results:

$$\begin{array}{r} 60.871 \\ 60.881 \\ 60.875 \\ \hline \text{Mean, } 60.8757, \pm .0020 \end{array}$$

In the second series the oxygen was passed through a weighed tube containing moist cotton, and another filled with pumice stone and sulphuric acid. Particles were thus collected which in the earlier series escaped. From these experiments we get—

$$\begin{array}{r} 60.947 \\ 60.947 \\ 60.952 \\ \hline \text{Mean, } 60.9487, \pm .0011 \end{array}$$

These last results were afterwards sharply criticised by Marignac,† and their value seriously questioned.

The next series, in order of time, is due to Maumené.‡ This chemist supposed that particles of chlorate, mechanically carried away, might continue to exist as chlorate, undecomposed; and hence that all previous series of experiments might give too high a value to the residual chloride. In his determinations, therefore, the ignition tube, after expulsion of the oxygen, was uniformly heated in all its parts. Here are his percentages of residue:

$$\begin{array}{r} 60.788 \\ 60.790 \\ 60.793 \\ 60.791 \\ 60.785 \\ 60.795 \\ 60.795 \\ \hline \text{Mean, } 60.791, \pm .0009 \end{array}$$

The question which most naturally arises in connection with these results is, whether portions of chloride may not have been volatilized, and so lost.

\* Compt. Rend., 21, 1280.

† Supp. Bibl. Univ. de Genève, Vol. I.

‡ Ann. d. Chim. et d. Phys. (3), 18, 71. 1846.



Closely following Maumené's paper, there is a short note by Faget,\* giving certain mean results. According to this chemist, when potassium chlorate is ignited slowly, we get 60.847 per cent. of residue. When the ignition is rapid, we get 60.942. As no detailed experiments are given, these figures can have no part in our discussion.

Last of all we have two series determined by Stas.† In the first series are the results obtained by igniting the chlorate. In the second series the chlorate was reduced by strong hydrochloric acid, after the method followed by Penny :

*First Series.*

60.8380	
60.8395	
60.8440	
60.8473	
60.8450	
<hr/>	
Mean,	60.84276, $\pm .0012$

*Second Series.*

60.850
60.853
60.844
<hr/>
Mean, 60.849, $\pm .0017$

In these experiments every conceivable precaution was taken to avoid error and insure accuracy. All weighings were reduced to a vacuum standard; from 70 to 142 grammes of chlorate were used in each experiment; and the chlorine carried away with the oxygen in the first series was absorbed by finely divided silver and estimated. It is difficult to see how any error could have occurred.

Now, to combine these different series of experiments.

Berzelius, mean result	60.851, $\pm .0006$
Penny,        "	60.8225, $\pm .0014$
Pelouze,       "	60.843, $\pm .0053$
Marignac,     "	60.8392, $\pm .0013$
Gerhardt, 1st "	60.8757, $\pm .0020$
"     2d "	60.9487, $\pm .0011$
Maumené,     "	60.791, $\pm .0009$
Stas, 1st       "	60.8428, $\pm .0012$
"     2d   "	60.849, $\pm .0017$

General mean from all nine series,  
representing forty experiments. . . . 60.846,  $\pm .00038$

This value is exactly that which Stas deduced from both of his own series combined, and gives great emphasis to his wonderfully accurate

\* Ann. d. Chim. et d. Phys. (3), 18, 80. 1846.

† See Aronstein's translation, p. 249.

work. It also finely illustrates the compensation of errors which occurs in combining the figures of different experimenters.

Similar analyses of silver chlorate have been made by Marignac and by Stas. Marignac's data are as follows: \* The third column gives the percentage of O in  $\text{AgClO}_3$ :

24.510 gm.	$\text{AgClO}_3$ gave	18.3616	$\text{AgCl}$ .	25.103
25.809	"	19.3345	"	25.086
30.306	"	22.7072	"	25.074
28.358	"	21.2453	"	25.082
28.287	"	21.1833	"	25.113
57.170	"	42.8366	"	25.072
				Mean, 25.088, $\pm .0044$

Stas † found the following percentages in two experiments only:

25.081
25.078
Mean, 25.0795, $\pm .0010$

Combined with Marignac's mean this gives a general mean of 25.080,  $\pm .0010$ ; that is, Marignac's series practically vanishes.

For the direct ratio between silver and chlorine there are seven available series of experiments. Here, as in many other ratios, the first reliable work was done by Berzelius. ‡

He made three estimations, using each time twenty grammes of pure silver. This was dissolved in nitric acid. In the first experiment the silver chloride was precipitated and collected on a filter. In the second and third experiments the solution was mixed with hydrochloric acid in a flask, evaporated to dryness, and the residue then fused and weighed without transfer. One hundred parts of silver formed of chloride:

132.700
132.780
132.790
Mean, 132.757, $\pm .019$

Turner's work § closely resembles that of Berzelius. Silver was dissolved in nitric acid and precipitated as chloride. In experiments one, two, and three the mixture was evaporated and the residue fused. In experiment four the chloride was collected on a filter. A fifth experiment was made, but has been rejected as worthless.

The results were as follows: In a third column I put the quantity of  $\text{AgCl}$  proportional to 100 parts of  $\text{Ag}$ .

\* Bibl. Univ. de Genève, 46, 356. 1843.

† Aronstein's translation, p. 214.

‡ Thomson's *Annals of Philosophy*, 1820, v. 15, 89.

§ Phil. Transactions, 1829, 291.

28.407 grains Ag gave	37.737 AgCl.	132.844
41.917       "       "	55.678       "	132.829
40.006       "       "	53.143       "	132.837
30.922       "       "	41.070       "	132.818

Mean, 132.832,  $\pm .0038$

The same general method of dissolving silver in nitric acid, precipitating, evaporating, and fusing without transfer of material was also adopted by Penny.\* His results for 100 parts of silver are as follows, in parts of chloride:

132.836
132.840
132.830
132.840
132.840
132.830
132.838

Mean, 132.8363,  $\pm .0012$

In 1842 Marignac† found that 100 parts of silver formed 132.74 of chloride, but gave no available details. Later,‡ in another series of determinations, he is more explicit, and gives the following data. The weighings were reduced to a vacuum standard:

79.853 grm. Ag gave	106.080 AgCl.	Ratio, 132.844
69.905       "       "	92.864       "	132.843
64.905       "       "	86.210       "	132.825
92.362       "       "	122.693       "	132.839
99.653       "       "	132.383       "	132.844

Mean, 132.839,  $\pm .0024$

The above series all represent the synthesis of silver chloride. Mau-  
mené§ made analyses of the compound, reducing it to metal in a current  
of hydrogen. His experiments make 100 parts of silver equivalent to  
chloride:

132.734
132.754
132.724
132.729
132.741

Mean, 132.7364,  $\pm .0077$

By Dumas|| we have the following estimations:

9.954 Ag gave	13.227 AgCl.	Ratio, 132.882
19.976       "       "	26.542       "	132.869

Mean, 132.8755,  $\pm .0044$

\*Phil. Transactions, 1839, 28.

†Ann. Chem. Pharm., 44, 21.

‡See Berzelius' Lehrbuch, 5th Ed., Vol. 3, pp. 1192, 1193.

§Ann. d. Chim. et d. Phys. (3), 18, 49. 1845.

||Ann. Chem. Pharm., 113, 21. 1860.

Finally, there are seven determinations by Stas,\* made with his usual accuracy and with every precaution against error. In the first, second, and third, silver was heated in chlorine gas, and the synthesis of silver chloride thus effected directly. In the fourth and fifth silver was dissolved in nitric acid, and the chloride thrown down by passing hydrochloric acid gas over the surface of the solution. The whole was then evaporated in the same vessel, and the chloride fused, first in an atmosphere of hydrochloric acid, and then in a stream of air. The sixth synthesis was similar to these, only the nitric solution was precipitated by hydrochloric acid in slight excess, and the chloride thrown down was washed by repeated decantation. All the decanted liquids were afterwards evaporated to dryness, and the trace of chloride thus recovered was estimated in addition to the main mass. The latter was fused in an atmosphere of HCl. The seventh experiment was like the sixth, only ammonium chloride was used instead of hydrochloric acid. From 98.3 to 399.7 grammes of silver were used in each experiment, the operations were performed chiefly in the dark, and all weighings were reduced to vacuum. In every case the chloride obtained was beautifully white. The following are the results in chloride for 100 of silver:

132.841
132.843
132.843
132.849
132.846
132.848
122.8417
<hr/>
Mean, 132.8445, $\pm .0008$

We may now combine the means of these seven series, representing in all thirty-three experiments. One hundred parts of silver are equivalent to chlorine, as follows:

Berzelius.....	32.757, $\pm .0190$
Turner.....	32.832, $\pm .0038$
Penny.....	32.8363, $\pm .0012$
Marignac.....	32.839, $\pm .0024$
Maumené.....	32.7364, $\pm .0077$
Dumas.....	32.8755, $\pm .0044$
Stas.....	32.8445, $\pm .0008$
<hr/>	
General mean....	32.8418, $\pm .0006$

Here, again, we have a fine example of the evident compensation of errors among different series of experiments. We have also another tribute to the accuracy of Stas, since this general mean varies from the mean of his results only within the limits of his own variations.

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\* Aronstein's translation, p. 171.

The ratio between silver and potassium chloride, or, in other words, the weight of silver in nitric acid solution which can be precipitated by a known weight of KCl, has been fixed by Marignac and by Stas. Marignac,\* reducing all weighings to vacuum, obtained these results. In the third column I give the weight of KCl proportional to 100 parts of Ag:

4.7238	gm.	Ag =	3.2626	KCl.	69.067
22.725	"	15.001	"		69.050
21.759	"	15.028	"		69.066
21.909	"	15.131	"		69.063
22.032	"	15.216	"		69.063
25.122	"	17.350	"		69.063

Mean, 69.062,  $\pm$  .0017

The work of Stas falls into several series, widely separated in point of time. His earlier experiments† upon this ratio may be divided into two sets, as follows: In the first set the silver was slightly impure, but the impurity was of known quantity, and corrections could therefore be applied. In the second series pure silver was employed. The potassium chloride was from several different sources, and in every case was purified with the utmost care. From 10.8 to 32.4 grammes of silver were taken in each experiment, and the weighings were reduced to vacuum. The method of operation was, in brief, as follows: A definite weight of potassium chloride was taken, and the exact quantity of silver necessary, according to Prout's hypothesis, to balance it was also weighed out. The metal, with suitable precautions, was dissolved in nitric acid, and the solution mixed with that of the chloride. After double decomposition the trifling excess of silver remaining in the liquid was determined by titration with a normal solution of potassium chloride. One hundred parts of silver required the following of KCl:

*First Series.*

69.105  
69.104  
69.103  
69.104  
69.102

Mean, 69.1036,  $\pm$  .0003

*Second Series.*

69.105  
69.099  
69.107  
69.103  
69.103  
69.105  
69.104

\* See Berzelius' *Lehrbuch*, 5th Ed., Vol. 3, pp. 1192-3.

† Aronstein's translation, pp. 250-257.

69.099
69.1034
69.104
69.103
69.102
69.104
69.104
69.105
69.103
69.101
69.105
69.103
Mean, 69.1033, $\pm .0003$

In these determinations Stas did not take into account the slight solubility of precipitated silver chloride in the menstrua employed in the experiments. Accordingly, in 1882\* he published a new series, in which by two methods he remeasured the ratio, guarding against the indicated error, and finding the following values :

69.1198
69.11965
69.121
69.123
Mean, 69.1209, $\pm .0003$

Corrected for a minute trace of silica contained in the potassium chloride, this mean becomes

$$69.11903, \pm .0003. \dagger$$

Still later, in order to establish the absolute constancy of the ratio in question, Stas made yet another series of determinations,‡ in which he employed potassium chloride prepared from four different sources. One lot of silver was used throughout. The values obtained were as follows :

69.1227
69.1236
69.1234
69.1244
69.1235
69.1228
69.1222
69.1211
69.1219
69.1249
69.1238
69.1225
69.1211

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\* Mémoires Acad. Roy. de Belge, t. 43. 1882.

† See Van der Plaats, Ann. Chim. Phys. (6), 7, 15.

‡ Oeuvres Posthumes, edited by W. Spring.

A series was also begun in which one sample of potassium chloride was to be balanced against silver from various sources, but only one result is given, namely, 69.1240. This, with the previous series, gives a mean of 69.1230,  $\pm .0002$ .

Five series of determinations are now at hand for the ratio Ag : KCl. They combine as follows :

Marignac.....	69.062, $\pm .0017$
Stas, 1st series.....	69.1036, $\pm .0003$
“ 2d “.....	69.1033, $\pm .0003$
“ 3d “.....	69.1190, $\pm .0003$
“ 4th “.....	69.1230, $\pm .0002$
<hr/>	
General mean.....	69.1143, $\pm .00013$

The difference between the highest and the lowest of Stas' series corresponds to a difference of 0.021 in the atomic weight of potassium. The rejection of the earlier work might be quite justifiable, but would exert a very slight influence upon our final result.

The quantity of silver chloride which can be formed from a known weight of potassium chloride has also been determined by Berzelius, Marignac and Maumené. Berzelius\* found that 100 parts of KCl were equivalent to 194.2 of AgCl; a value which, corrected for weighings in air, becomes 192.32. This experiment will not be included in our discussion.

In 1842 Marignac† published two determinations, with these results from 100 KCl :

192.33  
192.34

Mean, corrected for weighing in air, 192.26,  $\pm .003$

In 1846 Marignac‡ published another set of results, as follows. The weighings were reduced to vacuum. The usual ratio is in the third column :

17.034 grm. KCl gave	32.761 AgCl.	192.327
14.427 “	27.749 “	192.341
15.028 “	28.910 “	192.374
15.131 “	29.102 “	192.334
15.216 “	29.271 “	192.370

Mean, 192.349,  $\pm .006$

Three estimations of the same ratio were also made by Maumené§ as follows :

\* Poggend. Annal., 8, 1. 1826.

† Ann. Chem. Pharm., 44, 21, 1842.

‡ Berzelius' Lehrbuch, 5th Ed., Vol. 3, pp. 1192, 1193.

§ Ann. d. Chim. et d. Phys. (3), 18, 41. 1846.

10.700 gm. KCl gave	20.627 AgCl,	192.776
10.5195       “	20.273       “	192.716
8.587         “	16.556       “	192.803
		<hr/>
		Mean, 192.765, $\pm .017$

The three series of ten experiments in all foot up thus:

Marignac, 1842.....	192.260, $\pm .003$
“       1846.....	192.349, $\pm .006$
Maumené.....	192.765, $\pm .017$
<hr/>	
General mean.....	192.294, $\pm .0029$

These figures show clearly that the ratio which they represent is not of very high importance. It might be rejected altogether without impropriety, and is only retained for the sake of completeness. It will obviously receive but little weight in our final discussion.

In estimating the atomic weight of bromine the earlier experiments of Balard, Berzelius, Liebig, and Löwig may all be rejected. Their results were all far too low, probably because chlorine was present as an impurity in the materials employed. Wallace's determinations, based upon the analysis of arsenic tribromide, are tolerably good, but need not be considered here. In the present state of our knowledge, Wallace's analyses are better fitted for fixing the atomic weight of arsenic, and will, therefore, be discussed with reference to that element.

The ratios with which we now have to deal are closely similar to those involving chlorine. In the first place, there are the analyses of silver bromate by Stas.\* In two careful experiments he found in this salt the following percentages of oxygen:

20.351
20.347
<hr/>
Mean, 20.349, $\pm .0014$

There are also four analyses of potassium bromate by Marignac.† The salt was heated, and the percentage loss of oxygen determined. The residual bromide was feebly alkaline. We cannot place much reliance upon this series. The results are as follows:

28.7016
28.6496
28.6050
28.7460
<hr/>
Mean, 28.6755, $\pm .0207$

\* Aronstein's translation, pp. 200-206.

† See E. Mulder's *Overzicht*, p. 117; or Berzelius' *Jahresbericht*, 24, 72.



When silver bromide is heated in chlorine gas, silver chloride is formed. In 1860 Dumas\* employed this method for estimating the atomic weight of bromine. His results are as follows. In the third column I give the weight of AgBr equivalent to 100 parts of AgCl:

2.028	grm. AgBr gave	1.547	AgCl.	131.092
4.237	"	3.235	"	130.974
5.769	"	4.403	"	131.024
				<hr/>
				Mean, 131.030, $\pm .023$

This series is evidently of but little value.

The two ratios upon which, in connection with Stas' analyses of silver bromate, the atomic weight of bromine chiefly depends, are those which connect silver with the latter element directly and silver with potassium bromide.

Marignac,† to effect the synthesis of silver bromide, dissolved the metal in nitric acid, precipitated the solution with potassium bromide, washed, dried, fused, and weighed the product. The following quantities of bromine were found proportional to 100 parts of silver:

74.072
74.055
74.066
<hr/>

Mean, reduced to a vacuum standard, 74.077,  $\pm .003$

Much more elaborate determinations of this ratio are due to Stas.‡ In one experiment a known weight of silver was converted into nitrate, and precipitated in the same vessel by pure hydrobromic acid. The resulting bromide was washed thoroughly, dried, and weighed. In four other estimations the silver was converted into sulphate. Then a known quantity of pure bromine, as nearly as possible the exact amount necessary to precipitate the silver, was transformed into hydrobromic acid. This was added to the dilute solution of the sulphate, and, after precipitation was complete, the minute trace of an excess of silver in the clear supernatant fluid was determined. All weighings were reduced to a vacuum. From these experiments, taking both series as one, we get the following quantities of bromine corresponding to 100 parts of silver:

74.0830
<hr/>
74.0790
74.0795
74.0805
74.0830
<hr/>

Mean, 74.081,  $\pm .0006$

\* Ann. Chem. Pharm., 113, 20.

† E. Mulder's Overzicht, p. 116. Berzelius' Jahresbericht, 24, 72.

‡ Aronstein's translation, pp. 154-170.

In his paper on the atomic weight of cadmium,\* Huntington gives three syntheses and three analyses of silver bromide. The data are as follows, with the usual ratio given in the last column:

1.4852 gm. Ag gave	2.5855 AgBr.	74.084
1.4080           "	2.4510   "	74.077
1.4449           "	2.5150   "	74.060
4.1450 gm. AgBr gave	2.3817 Ag.	74.035
1.8172           "	1.0437   "	74.111
4.9601           "	2.8497   "	74.057

Mean, 74.071,  $\pm .0072$

Similar synthetic data are also given by Richards, incidentally to his work on copper.† There are two sets of three experiments each, which can here be treated as one series, thus:

{	1.11235 gm. Ag gave	1.93630 AgBr.	74.073
	1.57620           "	2.74335   "	74.044
	2.16670           "	3.77170   "	74.076
{	.9664           "	1.68205   "	74.053
	.9645           "	1.6789   "	74.069
	.9639           "	1.6779   "	74.074

Mean, 74.065,  $\pm .0035$

Another set of data by Richards appears in his research upon the atomic weight of barium;‡ in which BaBr<sub>2</sub> was balanced against silver, and the AgBr was also weighed. Richards gives from these data the percentage of Ag in AgBr, which figures are easily restated in the usual form as follows:

<i>Percentage.</i>	<i>Ratio.</i>
57.460	74.034
57.455	74.049
57.447	74.073
57.445	74.074
57.448	74.070
57.442	74.089
57.451	74.061
57.455	74.049
57.443	74.086
57.445	74.074
57.445	74.074

Mean, 74.067,  $\pm .0034$

The same ratio can also be computed indirectly from Cooke's experiments upon SbBr<sub>3</sub>, Huntington's on CdBr<sub>2</sub>, Thorpe's on TiBr<sub>4</sub>, and

\* Proc. Amer. Acad., 1881.

† Proc. Amer. Acad., 25, pp. 199, 210, 211. 1890.

‡ Proc. Amer. Acad., vol. 28. 1893.

Thorpe and Laurie's on gold. The values so obtained all confirm the results already given, varying within their limits, but having probable errors so high that their use would not affect the final mean. The latter is obtained as follows:

Marignac.....	74.077, $\pm$ .0030
Stas.....	74.081, $\pm$ .0006
Huntington.....	74.071, $\pm$ .0072
Richards, 1st series.....	74.065, $\pm$ .0035
"    2d    ".....	74.067, $\pm$ .0034
General mean....	<u>74.080, <math>\pm</math> .00057</u>

In this case again, as in so many others, Stas' work alone appears at the end, the remaining data having only corroborative value.

The ratio between silver and potassium bromide was first accurately determined by Marignac.\* I give, with his weighings, the quantity of KBr proportional to 100 parts of Ag:

2.131 gm. Ag =	2.351 KBr.	110.324
2.559    "	2.823    "	110.316
2.447    "	2.700    "	110.339
3.025    "	3.336    "	110.283
3.946    "	4.353    "	110.314
11.569    "	12.763    "	110.321
20.120    "	22.191    "	<u>110.293</u>

Mean, corrected for weighing in air, 110.343,  $\pm$  .005

Stas,† working in essentially the same manner as when he fixed the ratio between potassium chloride and silver, obtained the following results:

110.361
110.360
110.360
110.342
110.346
110.338
110.360
110.336
110.344
110.332
110.343
110.357
110.334
<u>110.335</u>

Mean, 110.3463,  $\pm$  .0020

Combining this with Marignac's mean result, 110.343.  $\pm$  .005, we get a general mean of 110.3459,  $\pm$  .0019.

\* Berzelius' Jahresbericht, 24, 72.

† Aronstein's translation, pp. 334-347.

The ratios upon which we must depend for the atomic weight of iodine are exactly parallel to those used for the determination of bromine.

To begin with, the percentage of oxygen in potassium iodate has been determined by Millon.\* In three experiments he found :

22.46
22.49
22.47
<hr/>
Mean, 22.473, $\pm .005$

Millon also estimated the oxygen in silver iodate, getting the following percentages :

17.05
17.03
17.06
<hr/>
Mean, 17.047, $\pm .005$

The analysis of silver iodate has also been performed with extreme care by Stas.† From 76 to 157 grammes were used in each experiment, the weights being reduced to a vacuum standard. As the salt could not be prepared in an absolutely anhydrous condition, the water expelled in each analysis was accurately estimated and the necessary corrections applied. In two of the experiments the iodate was decomposed by heat, and the oxygen given off was fixed upon a weighed quantity of copper heated to redness. Thus the actual weights, both of the oxygen and the residual iodide, were obtained. In a third experiment the iodate was reduced to iodide by a solution of sulphurous acid, and the oxygen was estimated only by difference. In the three percentages of oxygen given below, the result of this analysis comes last. The figures for oxygen are as follows :

16.976
16.972
16.9761
<hr/>
Mean, 16.9747, $\pm .0009$

This, combined with Millon's series above cited, gives us a general mean of 16.9771,  $\pm .0009$ .

The ratio between silver and potassium iodide seems to have been determined only by Marignac,‡ and without remarkable accuracy. In five experiments 100 parts of silver were found equivalent to potassium iodide as follows :

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\* Ann. Chim. Phys. (3), 9, 400. 1843.

† Aronstein's translation, pp. 170-200.

‡ Berzelius' Lehrbuch, 5th ed., 3, 1196.

1.616	gram.	Ag =	2.483	KI.	Ratio,	153.651
2.503	"		3.846	"	"	153.665
3.427	"		5.268	"	"	153.720
2.141	"		3.290	"	"	153.667
10.821	"		16.642	"	"	153.794
						<hr/>
						Mean, 153.6994, $\pm .0178$

The synthesis of silver iodide has been effected by both Marignac and Stas. Marignac, in the paper above cited, gives these weighings. In the last column I add the ratio between iodine and 100 parts of silver:

15.000	gm.	Ag gave	31.625	AgI.	117.500
14.790	"		32.170	"	117.512
18.545	"		40.339	"	117.519
					<hr/>
Mean, corrected for weighing in air,					117.5335, $\pm .0036$

Stas\* in his experiments worked after two methods, which gave, however, results concordant with each other and with those of Marignac.

In the first series of experiments Stas converted a known weight of silver into nitrate, and then precipitated with pure hydriodic acid. The iodide thus thrown down was washed, dried, and weighed without transfer. By this method 100 parts of silver were found to require of iodine:

117.529
117.536
<hr/>
Mean, 117.5325, $\pm .0024$

In the second series a complete synthesis of silver iodide from known weights of iodine and metal was performed. The iodine was dissolved in a solution of ammonium sulphite, and thus converted into ammonium iodide. The silver was transformed into sulphate and the two solutions were mixed. When the precipitate of silver iodide was completely deposited the supernatant liquid was titrated for the trifling excess of iodine which it always contained. As the two elements were weighed out in the ratio of 127 to 108, while the atomic weight of iodine is probably a little under 127, this excess is easily explained. From these experiments two sets of values were deduced; one from the weights of silver and iodine actually employed, the other from the quantity of iodide of silver collected. From the first set we have of iodine for 100 parts of silver:

117.5390
117.5380
117.5318
117.5430
117.5420
117.5300
<hr/>
Mean, 117.5373, $\pm .0015$

---

\* Aronstein's translation, pp. 136, 152.

From the weight of silver iodide actually collected we get as follows. For experiment number three in the above column there is no equivalent here :

117.529
117.531
117.539
117.538
• 117.530
<hr/>
Mean, 117.5334, $\pm .0014$

Now, combining these several sets of results, we have the following general mean :

Maignac.....	117.5335, $\pm .0036$
Stas, 1st series.....	117.5325, $\pm .0024$
“ 2d “ .....	117.5373, $\pm .0015$
“ 3d “ .....	117.5334, $\pm .0014$
<hr/>	
General mean.....	117.5345, $\pm .0009$

One other comparatively unimportant iodine ratio remains for us to notice. Silver iodide, heated in a stream of chlorine, becomes converted into chloride; and the ratio between these two salts has been thus determined by Berzelius and by Dumas.

From Berzelius\* we have the following data. In the third column I give the ratio between AgI and 100 parts of AgCl :

5.000 gm. AgI gave 3.062 AgCl.	163.292
12.212 “ 7.4755 “	163.360
<hr/>	
Mean, 163.326, $\pm .023$	

Dumas'† results were as follows :

3.520 gm. AgI gave 2.149 AgCl.	163.793
7.011 “ 4.281 “	163.770
<hr/>	
Mean, 163.782, $\pm .008$	

General mean from the combination of both series, 163.783,  $\pm .0076$ .

For sodium there are but four ratios of any value for present purposes.

The early work of Berzelius we may disregard entirely, and confine ourselves to the consideration of the results obtained by Penny, Pelouze, Dumas, and Stas, together with a single ratio measured incidentally by Ramsay and Aston.

The percentage of oxygen in sodium chlorate has been determined only by Penny‡, who used the same method which he applied to the potassium salt. Four experiments gave the following results :

\* Ann. Chim. Phys. (2), 40, 430. 1829.

† Ann. Chem. Pharm., 113, 28. 1860.

‡ Phil. Transactions, 1839, p. 25.

45.060  
 45.075  
 45.080  
45.067

Mean, 45.0705,  $\pm .0029$ .

The ratio between silver and sodium chloride has been fixed by Pelouze, Dumas, and Stas. Pelouze\* dissolved a weighed quantity of silver in nitric acid, and then titrated with sodium chloride. Equivalent to 100 parts of silver he found of chloride:

54.158  
 54.125  
54.139

Mean, 54.141,  $\pm .0063$

By Dumas† we have seven experiments, with results as follows. The third column gives the ratio between 100 of silver and NaCl:

2.0535	gram. NaCl =	3.788	gram. Ag.	54.211
2.169	"	4.0095	"	54.097
4.3554	"	8.0425	"	54.155
6.509	"	12.0140	"	54.178
6.413	"	11.8375	"	54.175
2.1746	"	4.012	"	54.202
5.113	"	9.434	"	<u>54.187</u>

Mean, 54.172,  $\pm .0096$

Stas,‡ applying the method used in establishing the similar ratio for potassium chloride, and working with salt from six different sources, found of sodium chloride equivalent to 100 parts of silver:

54.2093  
 54.2088  
 54.2070  
 54.2070  
 54.2070  
 54.2060  
 54.2076  
 54.2081  
 54.2083  
54.2089

Mean, 54.2078,  $\pm .0002$

As in the case of the corresponding ratio for potassium chloride, these data needed to be checked by others which took into account the solu-

\*Compt. Rend., 20, 1047. 1845.

†Ann. Chem. Pharm., 113, 31. 1860.

‡Aronstein's translation, p. 274.

bility of silver chloride. Such data are given in Stas' paper of 1882,\* and four results are as follows :

54.2065
54.20676
54.2091
54.2054
<hr/>
Mean, 54.20694, $\pm .00045$

Corrected for a trace of silica in the sodium chloride, this mean becomes 54.2046,  $\pm .00045$ .† Combining all four series, we have for the NaCl equivalent to 100 parts of Ag—

Pelouze .....	54.141, $\pm .0063$
Dumas.....	54.172, $\pm .0096$
Stas, early series.....	54.2078, $\pm .0002$
Stas, late “ .....	54.2046, $\pm .00045$
<hr/>	
General mean.....	54.2071, $\pm .00018$

Here the work of Stas is of such superior excellence that the other determinations might be completely rejected without appreciably affecting our final results.

In their research upon the atomic weight of boron, Ramsay and Aston ‡ converted borax into sodium chloride. In the latter the chlorine was afterwards estimated gravimetrically by weighing as silver chloride on a Gooch filter. Hence the ratio, AgCl : NaCl : : 100 :  $x$ , as follows :

3.0761	gram. NaCl gave	7.5259	AgCl.	Ratio, 40.874
2.7700	“	6.7794	“	“ 40.859
2.8930	“	7.0804	“	“ 40.859
2.7360	“	6.6960	“	“ 40.860
1.9187	“	4.6931	“	“ 40.863
<hr/>				
Mean, 40.867, $\pm .0033$				

Finally, for the ratios between silver and sodium bromide we have one set of measurements by Stas.§ The bromide was prepared by saturating  $\text{Na}_2\text{CO}_3$  with HBr. The NaBr proportional to 100 parts of silver was—

95.4420
95.4383
95.4426
95.4392
<hr/>
Mean, 95.4405, $\pm .0007$

We have now before us the data for computing, with greater or less accuracy, the atomic weights of the six elements under discussion. In

\* Mémoires Acad. Roy. de Belge., 43. 1882.

† See Van der Plaats, Ann. Chim. Phys. (6), 7, 16. 1886.

‡ Chem. News, 66, 92. 1892.

§ Mémoires Acad. Roy. Belge., 43. 1882.



all there are nineteen ratios, involving about two hundred and fifty separate experiments. These ratios may now be tabulated and numbered for reference, it being understood that the probable error in each case is that of the last term in the proportion.

- (1.) Percentage of O in  $\text{KClO}_3$  . . . . . 39.154,  $\pm .00038$
- (2.)     "     "      $\text{KBrO}_3$  . . . . . 28.6755,  $\pm .0207$
- (3.)     "     "      $\text{KIO}_3$  . . . . . 22.473,  $\pm .0050$
- (4.)     "     "      $\text{NaClO}_3$  . . . . . 45.0705,  $\pm .0029$
- (5.)     "     "      $\text{AgClO}_3$  . . . . . 25.080,  $\pm .0010$
- (6.)     "     "      $\text{AgBrO}_3$  . . . . . 20.349,  $\pm .0014$
- (7.)     "     "      $\text{AgIO}_3$  . . . . . 16.9771,  $\pm .0009$
- (8.) Ag : NaCl : : 100 : 54.2071,  $\pm .00018$
- (9.) Ag : NaBr : : 100 : 95.4405,  $\pm .0007$
- (10.) Ag : KCl : : 100 : 69.1143,  $\pm .00013$
- (11.) Ag : KBr : : 100 : 110.3459,  $\pm .0019$
- (12.) Ag : KI : : 100 : 153.6994,  $\pm .0178$
- (13.) Ag : Cl : : 100 : 32.8418,  $\pm .0006$
- (14.) Ag : Br : : 100 : 74.080,  $\pm .00057$
- (15.) Ag : I : : 100 : 117.5345,  $\pm .0009$
- (16.) AgCl : NaCl : : 100 : 40.867,  $\pm .0033$
- (17.) KCl : AgCl : : 100 : 192.294,  $\pm .0029$
- (18.) AgCl : AgBr : : 100 : 131.030,  $\pm .023$
- (19.) AgCl : AgI : : 100 : 163.733,  $\pm .0076$

Now, from ratios 1 to 7, inclusive, we can at once, by applying the known atomic weight of oxygen, deduce the molecular weights of seven haloid salts. Let us consider the first calculation somewhat in detail.

Potassium chlorate yields 39.154 per cent. of oxygen and 60.846 per cent. of residual chloride. For each of these quantities the probable error is  $\pm .00038$ . The atomic weight of oxygen is 15.879,  $\pm .0003$ , so that the value for three atoms becomes 47.637,  $\pm .0009$ . We have now the following simple proportion :

$$39.154 : 60.846 : : 47.637 : x,$$

whence the molecular weight of potassium chloride becomes = 74.029.

The probable error being known for the first, second, and third term of this proportion, we can easily find that of the fourth term by the formula given in our introduction. It is  $\pm .0073$ . By this method we obtain the following series of values, which may conveniently be numbered consecutively with the foregoing ratios :

- (20) KCl, from (1) = 74.029,  $\pm .0073$
- (21) KBr,     "     (2) = 118.487,  $\pm .0923$
- (22) KI,     "     (3) = 164.337,  $\pm .0382$
- (23) NaCl,   "     (4) = 58.057,  $\pm .0050$
- (24) AgCl,   "     (5) = 142.303,  $\pm .0066$
- (25) AgBr,   "     (6) = 186.463,  $\pm .0137$
- (26) AgI,     "     (7) = 232.959,  $\pm .0134$

With the help of these molecular weights, we are now able to compute seven independent values for the atomic weight of silver.

First,	from (10) and (20)....	Ag = 107.111, $\pm$ .0106
Second,	" (11) " (21).....	" = 107.378, $\pm$ .0837
Third,	" (12) " (22).....	" = 106.921, $\pm$ .0278
Fourth,	" (8) " (23).....	" = 107.102, $\pm$ .0092
Fifth,	" (13) " (24).....	" = 107.122, $\pm$ .0050
Sixth,	" (14) " (25).....	" = 107.113, $\pm$ .0079
Seventh,	" (15) " (26).....	" = 107.091, $\pm$ .0062

---

General mean..... Ag = 107.108,  $\pm$  .0031

It is noticeable that five of these values agree very well. The second and third, however, diverge widely from the average, but in opposite directions; they have, moreover, high probable errors, and consequently little weight. Of these two, one represents little and the other none of Stas' work. Their trifling influence upon our final results becomes curiously apparent in the series of silver values given a little further along.

When we consider closely, in all of its bearings, any one of the values just given, we shall see that for certain purposes it must be excluded from our general mean. For example, the first is derived partly from the ratio between silver and potassium chloride. From this ratio, the atomic weight of one substance being known, we can deduce that of the other. We have already used it in ascertaining the atomic weight of silver, and the value thus obtained is included in our general mean. But if from it we are to determine the molecular weight of potassium chloride, we must use a silver value derived from other sources only, or we should be assuming a part of our result in advance. In other words, we must now use a general mean for silver from which this ratio with reference to silver has been rejected. Hence the following series of silver values, which are lettered for reference:

A.	General mean from all eight.....	107.108, $\pm$ .0031
B.	" excluding the first.....	107.108, $\pm$ .0032
C.	" " second.....	107.107, $\pm$ .0031
D.	" " third.....	107.110, $\pm$ .0031
E.	" " fourth.....	107.109, $\pm$ .0033
F.	" " fifth.....	107.099, $\pm$ .0039
G.	" " sixth.....	107.106, $\pm$ .0034
H.	" " seventh.....	107.113, $\pm$ .0036

We are now in a position to determine more closely the molecular weights of the haloid salts which we have already been considering.

For silver chloride, still employing the formula for the probable error of the last term of a proportion, we get the following values:

From (5).....	AgCl = 142.303, $\pm$ .0066
From (13) and (F).....	" = 142.276, $\pm$ .0052
From (16) " (23).....	" = 142.063, $\pm$ .0168
From (17) " (20).....	" = 142.353, $\pm$ .0156
From (18) " (25).....	" = 142.306, $\pm$ .0271
From (19) " (26).....	" = 142.278, $\pm$ .0105
<hr/>	
General mean.....	AgCl = 142.277, $\pm$ .0036

The third of these values is certainly too low, and although it reduces the atomic weight of chlorine by only 0.01, it ought to be rejected. The general mean of the other five values is  $\text{AgCl} = 142.287, \pm .0037$ . Subtracting from this the atomic weight of silver,  $107.108, \pm .0031$ , we have for the atomic weight of chlorine—

$$\text{Cl} = 35.179, \pm .0048.$$

For silver bromide three ratios are available:

From (6).....	AgBr = 186.463, $\pm$ .0137
From (14) and (G).....	" = 186.450, $\pm$ .0050
From (18) " (24).....	" = 186.459, $\pm$ .0339
<hr/>	
General mean.....	AgBr = 186.452, $\pm$ .0054

Hence, applying the atomic weight of silver as before—

$$\text{Br} = 79.344, \pm .0062.$$

For silver iodide we have—

From (7).....	AgI = 232.959, $\pm$ .0134
From (15) and (H).....	" = 233.008, $\pm$ .0079
From (19) " (24).....	" = 232.997, $\pm$ .0153
<hr/>	
General mean.....	AgI = 232.996, $\pm$ .0062

Hence,

$$\text{I} = 125.888, \pm .0069.$$

For the molecular weight of sodium chloride three values appear, as follows:

From (4).....	NaCl = 58.057, $\pm$ .0050
From (8) and (E).....	" = 58.061, $\pm$ .0018
From (16) " AgCl.....	" = 58.148, $\pm$ .0049
<hr/>	
General mean.....	NaCl = 58.069, $\pm$ .0016

Rejecting the third value, which corresponds to the rejected value for AgCl and throws out ratio (16) entirely, the mean becomes

$$\text{NaCl} = 58.060, \pm .0017$$

From (9) and (A).....	NaBr = 102.224, $\pm$ .0031
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Deducting from these molecular weights the values already found for Cl and Br, two measurements of the atomic weight of sodium are obtained, thus :

From NaCl.....	Na = 22.881, $\pm$ .0051
From NaBr.....	“ = 22.880, $\pm$ .0112
General mean.....	Na = 22.881, $\pm$ .0046

The rejection of ratio (16) in connection with the atomic weights of sodium and chlorine is fully justified by the fact that the data which it represents were never intended for use in such computations. They were obtained incidentally in connection with work upon boron, and their consideration here may have some bearing later upon the discussion of the last-named element.

For potassium, the ratios available give molecular weights for the chloride, bromide, and iodide. For the chloride,

From (1).....	KCl = 74.029, $\pm$ .0073
From (10) and (B).....	“ = 74.027, $\pm$ .0022
From (17) “ (24).....	“ = 74.003, $\pm$ .0049
General mean.....	KCl = 74.025, $\pm$ .0019

For the bromide we have—

From (2).....	KBr = 118.487, $\pm$ .0023
From (11) and (C).....	“ = 118.188, $\pm$ .0073
General mean.....	KBr = 118.200, $\pm$ .0073

And for the iodide—

From (3).....	KI = 164.337, $\pm$ .0382
From (12) and (D).....	“ = 164.627, $\pm$ .0052
General mean.....	KI = 164.622, $\pm$ .0051

Combining these values with those found for chlorine, bromine, and iodine, we have three values for the atomic weight of potassium, as follows :

From KCl.....	K = 38.846, $\pm$ .0078
From KBr.....	“ = 38.856, $\pm$ .0096
From KI.....	“ = 38.734, $\pm$ .0086
General mean.....	K = 38.817, $\pm$ .0051

To sum up, the six atomic weights under discussion may be tabulated as follows, both for the standard chosen, and with O = 16 as the base of the system :

	$H = 1.$	$O = 16.$
Ag.....	107.108, $\pm .0031$	107.924
K.....	38.817, $\pm .0051$	39.112
Na.....	22.881, $\pm .0046$	23.048
Cl... ..	35.179, $\pm .0048$	35.447
Br.....	79.344, $\pm .0062$	79.949
I.....	125.888, $\pm .0069$	126.847

It must be remembered that these values represent the summing up of work done by many investigators. Stas' ratios, taken by themselves, give various results, according to the method of combining them. This computation has been made by Stas himself, with his older determinations, and more recently by Ostwald,\* Van der Plaats,† and Thomsen,‡ all with the standard of  $O = 16$ . By Van der Plaats two sets of results are given: one with Stas' ratios assigned equal weight (A), and the other with each ratio given weight inversely proportional to the square of its mean error (B). The results of these several computations may well be tabulated in comparison with the values obtained in my own general discussion, thus:

	<i>Clarke.</i>	<i>Stas.</i>	<i>Ostwald.</i>	<i>V. der P., A.</i>	<i>V. der P., B.</i>	<i>Thomsen.</i>
Ag.....	107.924	107.930	107.9376	107.9202	107.9244	107.9299
K.....	39.112	39.137	39.1361	39.1414	39.1403	39.1507
Na.....	23.048	23.043	23.0575	23.0453	23.0443	23.0543
Cl.... .	35.447	35.457	35.4529	35.4516	35.4565	35.4494
Br.....	79.949	79.952	79.9628	79.9407	79.9548	79.9510
I.....	126.847	126.850	126.8640	126.8445	126.8494	126.8556

The agreement between the new values and the others is highly satisfactory, and gives a strong emphasis to the magnificent accuracy of Stas' determinations. No severer test could be applied to them.

\* Lehrbuch der allgemeinen Chemie, 1, 41. 1885.

† Compt. Rend., 116, 1362. 1893.

‡ Zeitsch. Physikal. Chem., 13, 726. 1894.

## NITROGEN.

The atomic weight of nitrogen has been determined from the density of the gas, and from a considerable variety of purely chemical ratios.

Upon the density of nitrogen a great many experiments have been made. In early times this constant was determined by Biot and Arago, Thomson, Dulong and Berzelius, Lavoisier, and others. But all of these investigations may be disregarded as of insufficient accuracy; and, as in the case of oxygen, we need consider only the results obtained by Dumas and Boussingault, by Regnault, and by recent investigators.

Taking air as unity, Dumas and Boussingault\* found the density of nitrogen to be—

$$\begin{array}{r} .970 \\ .972 \\ .974 \\ \hline \text{Mean, } .972, \pm .00078 \end{array}$$

For hydrogen, as was seen in our discussion of the atomic weight of oxygen, the same investigators found a mean of .0693,  $\pm .00013$ . Upon combining this with the above nitrogen mean, we find for the atomic weight of the latter element,  $N = 14.026, \pm .0295$ .

By Regnault † much closer work was done. He found the density of nitrogen to be as follows:

$$\begin{array}{r} .97148 \\ .97148 \\ .97154 \\ .97155 \\ .97108 \\ .97108 \\ \hline \text{Mean, } .97137, \pm .000062 \end{array}$$

For hydrogen, Regnault's mean value is .069263,  $\pm .000019$ . Hence, combining as before,  $N = 14.0244 \pm .0039$ .

Both of the preceding values are affected by a correction for the difference in volume between the weighing globes when full and when empty. This correction, in the case of Regnault's data, has been measured by Crafts, ‡ who gives .06949 for the density of H, and .97138 for N. Corrected ratio,  $N = 13.9787$ . If we assume the same proportional correction for the determination by Dumas and Boussingault, that becomes  $N = 13.9771$ .

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\* Compt. Rend., 12, 1005. 1841.

† Compt. Rend., 20, 975. 1845.

‡ Compt. Rend., 106, 1664.

Von Jolly,\* working with electrolytic oxygen and with nitrogen prepared by passing air over hot copper, but not with hydrogen, compared the weights of equal volumes of the two gases, with results as follows :

<i>Oxygen.</i>	<i>Nitrogen.</i>
1.442470	1.269609
1.442579	1.269389
1.442489	1.269307
1.442570	1.269449
1.442571	1.269515
1.442562	1.269443
1.442478	1.269478
Mean, 1.442545, $\pm .000013$	Mean, 1.269455, $\pm .000024$

The ratio, when  $O = 16$ , is  $N = 14.0802, \pm .0003$ . Corrected by Rayleigh, the ratio between the weights becomes 14.0805. If  $O = 15.879, \pm .0003$ , the final value for  $N$ , deducible from Von Jolly's data, is  $N = 13.974, \pm .0004$ .

The next determination in order of time is Leduc's.† He made nine measurements of the density of nitrogen, giving a mean of .97203, with extremes of .9719 and .9721; but he neglects to cite the intermediate values. Taking the three figures given as representative, and assuming a fair distribution of the other values between the indicated limits, the probable error of the mean is not far from 0.00002. For hydrogen he found .06948,  $\pm .00006745$ . The ratio between the two densities gives  $N = 13.9901, \pm .0138$ .

Lord Rayleigh,‡ preparing nitrogen by passing air over hot copper, and weighing in a standard globe, obtained the following weights :

2.31035
2.31026
2.31024
2.31012
2.31027
Mean, 2.31025, $\pm .000025$

With corrections for temperature, shrinkage of the globe when exhausted, etc., this becomes 2.30883, as against 2.37512 for the same volume of air. Hence the density of  $N = .97209, \pm .00001$ . His former work on hydrogen gives .06960,  $\pm .0000084$ , for the density of that gas. The ratio is  $N = 13.9678, \pm .0017$ .

The foregoing data, however, all apply to nitrogen derived from the atmosphere. In a later memoir Rayleigh§ found that nitrogen from

\* Poggend. Annalen (2), 6, 529-530. 1879.

† Compt. Rend., 113, 186. 1891.

‡ Proc. Roy. Soc., 53, 134. 1894.

§ Chem. News, 69, 231. 1894.

chemical sources, such as oxides of nitrogen, ammonium nitrate, etc., was perceptibly lighter; and not long afterwards the discrepancy was explained by the astonishing discovery of argon. The densities given, therefore, are all too high, and unavailable for any discussion of atomic weight. As, however, the reductions had been completed in nearly all their details before the existence of argon was announced, they may be allowed to remain here as part of the record. Summing up, the ratios found between hydrogen and atmospheric "nitrogen" are as follows:

Dumas and Boussingault, corrected.....	13.977
Regnault, " .....	13.979
Von Jolly, " ... ..	13.974
Leduc, " .....	13.990
Rayleigh, " .....	13.968

Perhaps at some future time, when the density of argon is accurately known and its amount in the atmosphere has been precisely determined, these figures may be so corrected as to be useful for atomic weight calculations.

In discussing the more purely chemical ratios for establishing the atomic weight of nitrogen, we may ignore, for the present, the researches of Berzelius and of Anderson. These chemists experimented chiefly upon lead nitrate, and their work is consequently now of greater value for fixing the atomic weight of lead. Their results will be duly considered in the proper connection further on.

The ratio between ammonium chloride and silver has been determined by Pelouze, by Marignac, and by Stas. The method of working is essentially that adopted in the similar experiments with the chlorides of sodium and potassium.

For the ammonium chloride equivalent to 100 parts of silver, Pelouze\* found:

$$\begin{array}{r} 49.556 \\ 49.517 \\ \hline \text{Mean, } 49.5365, \pm .013 \end{array}$$

Marignac† obtained the following results. The usual ratio for 100 parts of silver is given also:

8.063	gram.	Ag =	3.992	gram.	NH <sub>4</sub> Cl.	49.510
9.402	"		4.656	"	"	49.521
10.339	"		5.120	"	"	49.521
12.497	"		6.191	"	"	49.540
11.337	"		5.617	"	"	49.546
11.307	"		5.595	"	"	49.483
4.326	"		2.143	"	"	49.538
						<u>49.533</u>
						Mean, 49.523, $\pm .0055$

\* Compt. Rend., 20, 1047. 1845.

† Berzelius' Lehrbuch, 5th ed., vol. 3, 1184, 1185.



But neither of these series can for a moment compare with that of Stas.\* He used from 12.5 to 80 grammes of silver in each experiment, reduced his weighings to a vacuum standard, and adopted a great variety of precautions to insure accuracy. He found for every 100 parts of silver the following quantities of  $\text{NH}_4\text{Cl}$ :

49.600
49.599
49.597
49.598
49.597
49.593
49.597
49.5974
49.602
49.597
49.598
49.592

Mean, 49.5973,  $\pm .0005$

In this work, as with the similar ratios for potassium and sodium chloride, the solubility of silver chloride was not guarded against so fully as is needful. Accordingly Stas published a new series of determinations in 1882,† carefully checked in this particular, with the subjoined values for the ratio:

49.60001
49.59999
49.599
49.600
49.597

Mean, 49.5992,  $\pm .00039$

Combining all four series, we have—

Pelouze .....	49.5365, $\pm .013$
Marignac.....	49.523, $\pm .0055$
Stas, early series.....	49.5973, $\pm .0005$
Stas, later “ .....	49.5992, $\pm .00039$
General mean.....	49.5983, $\pm .00031$

In the paper last cited Stas also gives a similar series of determinations for the ratio  $\text{Ag} : \text{NH}_4\text{Br} :: 100 : x$ . The results are as follows, with reduction to vacuum:

\* Aronstein's translation, pp. 56-58.

† Mémoires Acad. Roy. de Belge., 43. 1882.

90.831  
 90.831  
 90.8297  
 90.823  
 90.8317  
 90.8311  
 90.832

Mean, 90.8299,  $\pm .0008$

The quantity of silver nitrate which can be formed from a known weight of metallic silver has been determined by Penny, by Marignac, and by Stas. Penny\* dissolved silver in nitric acid in a flask, evaporated to dryness without transfer, and weighed. One hundred parts of silver thus gave of nitrate:

157.430  
 157.437  
 157.458  
 157.440  
 157.430  
 157.455

Mean, 157.4417,  $\pm .0033$

Marignac's† results were as follows. In the third column they are reduced to the common standard of 100 parts of silver:

68.987 grm. Ag gave	108.608 grm. AgNO <sub>3</sub> .	157.433
57.844	“ 91.047	157.401
66.436	“ 104.592	157.433
70.340	“ 110.718	157.404
200.000	“ 314.894	157.447

Mean, 157.4236,  $\pm .0061$

Stas,‡ employing from 77 to 405 grammes of silver in each experiment, made two different series of determinations at two different times. The silver was dissolved with all the usual precautions against loss and against impurity, and the resulting nitrate was weighed, first after long drying without fusion, just below its melting point; and again, fused. Between the fused and the unfused salt there was in every case a slight difference in weight, the latter giving a maximum and the former a minimum value.

In Stas' first series there are eight experiments; but the seventh he himself rejects as inexact. The values obtained for the nitrate from 100

\* Phil. Trans., 1839.

† Berzelius' Lehrbuch, 5th ed., 3, pp. 1184, 1185.

‡ Aronstein's translation, pp. 305 and 315.

parts of silver are given below in two columns, representing the two conditions in which the salt was weighed. The general mean given at the end I have deduced from the means of the two columns considered separately :

<i>Unfused.</i>	<i>Fused.</i>
157.492	157.474
157.510	157.481
157.485	157.477
157.476	157.471
157.478	157.470
157.471	157.463
157.488	157.469
Mean, 157.4857	Mean, 157.472
General mean, 157.474, $\pm .0014$	

In the later series there are but two experiments, as follows :

<i>Unfused.</i>	<i>Fused.</i>
157.4964	157.488
157.4940	157.480
Mean, 157.4952	Mean, 157.484
General mean, 157.486, $\pm .0003$	

The reverse ratio, namely, the amount of silver obtainable from a weighed quantity of nitrate, has been determined electrolytically by Hardin.\* The data obtained, however, are reducible to the same form as in the preceding series, and all are properly combinable together. Pure silver was dissolved in pure aqueous nitric acid, and the crystalline salt thus formed was dried, fused, and used for the determinations. The silver nitrate, mixed with an excess of pure potassium cyanide solution, was electrolyzed in a platinum dish. The results obtained, reduced to vacuum weights, were as follows :

.31202	AgNO <sub>3</sub> gave .19812	Ag.	Ratio, 157.490
.47832	"	.30370 "	" 157.498
.56742	"	.36030 "	" 157.485
.57728	"	.36655 "	" 157.490
.69409	"	.44075 "	" 157.479
.86367	"	.54843 "	" 157.479
.86811	"	.55130 "	" 157.466
.93716	"	.59508 "	" 157.485
1.06170	"	.67412 "	" 157.494
1.19849	"	.76104 "	" 157.477
Mean, 157.484, $\pm .0020$			

\* Journ. Amer. Chem. Soc., 18, 995. 1896.

Now, to combine all five sets of results :

Penny.....	157.4417, $\pm .0033$
Marignac.....	157.4236, $\pm .0061$
Stas, 1st series.....	157.4740, $\pm .0014$
Stas, 2d ".....	157.4860, $\pm .0003$
Hardin.....	157.484, $\pm .0020$
<hr/>	
General mean.....	157.479, $\pm .0003$

For the direct ratio between silver nitrate and silver chloride there are two series of estimations. A weighed quantity of nitrate is easily converted into chloride, and the weight of the latter ascertained. In two experiments Turner\* found of chloride from 100 parts of nitrate :

$$\begin{array}{r} 84.357 \\ 84.389 \\ \hline \text{Mean, } 84.373, \pm .011 \end{array}$$

Penny,† in five determinations, found the following percentages :

$$\begin{array}{r} 84.370 \\ 84.388 \\ 84.377 \\ 84.367 \\ 84.370 \\ \hline \text{Mean, } 84.3744, \pm .0025 \end{array}$$

The general mean from both series is  $84.3743, \pm .0025$ .

The ratio directly connecting silver nitrate with ammonium chloride has been determined only by Stas.‡ The usual method of working was followed, namely, nearly equivalent quantities of the two salts were weighed out, the solutions mixed, and the slight excess of one estimated by titration. In four experiments 100 parts of silver nitrate were found equivalent to chloride of ammonium, as follows :

$$\begin{array}{r} 31.489 \\ 31.490 \\ 31.487 \\ 31.486 \\ \hline \text{Mean, } 31.488, \pm .0006 \end{array}$$

The similar ratio between potassium chloride and silver nitrate has been determined by both Marignac and Stas.

\* Phil. Trans., 1833, 537.

† Phil. Trans., 1839.

‡ Aronstein's translation, p. 309.

Marignac\* gives the following weights. I add the quantity of KCl proportional to 100 parts of  $\text{AgNO}_3$ :

1.849	gram.	KCl =	4.218	gram.	$\text{AgNO}_3$ .	43.836
2.473		"	5.640		"	43.848
3.317		"	7.565		"	43.847
2.926		"	6.670		"	43.868
6.191		"	14.110		"	43.877
4.351		"	9.918		"	43.870

Mean, 43.858,  $\pm$  .0044

Stas'† results are given in three series, representing silver nitrate from three different sources. In the third series the nitrate was weighed in vacuo, while for the other series this correction was applied in the usual way. For the KCl equivalent to 100 parts of  $\text{AgNO}_3$  Stas found:

*First Series.*

43.878  
43.875  
43.875  
43.874

Mean, 43.8755,  $\pm$  .0005.

*Second Series.*

43.864  
43.869  
43.876

Mean, 43.8697,  $\pm$  .0023

*Third Series.*

43.894  
43.878  
43.885

Mean, 43.8857,  $\pm$  .0031

Combining all four series we have:

Marignac.....	43.858, $\pm$ .0044
Stas, 1st series.....	43.8755, $\pm$ .0005
Stas, 2d ".....	43.8697, $\pm$ .0023
Stas, 3d ".....	43.8857, $\pm$ .0031
General mean.....	<u>43.8715, <math>\pm</math> .0004</u>

There have also been determined by Penny, by Stas, and by Hibbs a series of ratios connecting the alkaline chlorides and chlorates with the corresponding nitrates. One of these, relating to the lithium salts, will be studied farther on with reference to that metal.

\* Berzelius' *Lehrbuch*, 5th ed., 3d vol., 1184, 1185.

† Aronstein's translation, p. 308.

The general method of working upon these ratios is due to Penny.\* Applied to the ratio between the chloride and nitrate of potassium, it is as follows: A weighed quantity of the chloride is introduced into a flask which is placed upon its side and connected with a receiver. An excess of pure nitric acid is added, and the transformation is gradually brought about by the aid of heat. Then, upon evaporating to dryness over a sand bath, the nitrate is brought into weighable form. The liquid in the receiver is also evaporated, and the trace of solid matter which had been mechanically carried over is recovered and also taken into account. In another series of experiments the nitrate was taken, and by pure hydrochloric acid converted into chloride, the process being the same. In the following columns of figures I have reduced both series to one standard, namely, so as to express the number of parts of nitrate corresponding to 100 of chloride:

*First Series.—KCl treated with HNO<sub>3</sub>.*

135.639
135.637
135.640
135.635
135.630
135.640
135.630
<hr/>
Mean, 135.636, $\pm .0011$

*Second Series.—KNO<sub>3</sub> treated with HCl.*

135.628
135.635
135.630
135.641
135.630
135.635
135.630
<hr/>
Mean, 135.633, $\pm .0011$

Stas' † results are as follows:

135.643	
135.638	
135.647	
135.649	
135.640	
135.645	
135.655	
<hr/>	
Mean, 135.6453, $\pm .0014$	

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\* Phil. Trans., 1839.

† Aronstein's translation, p. 270.

These figures by Stas represent weighings in the air. Reduced to a vacuum standard, this mean becomes 135.6423.

The determinations made by Hibbs\* differ slightly in method from those of Penny and Stas. He converted the nitrate into the chloride by heating in a stream of gaseous hydrochloric acid. His results were as follows, vacuum weights being given.

<i>Weight KNO<sub>3</sub></i>	<i>Weight KCl.</i>	<i>Ratio.</i>
.11090	.08177	135.624
.14871	.10965	135.622
.21067	.15533	135.627
.23360	.17225	135.620
.24284	.17903	135.642
		<hr/>
		Mean, 135.627, $\pm .0026$

Now, combining, we have:

Penny, 1st series.....	135.636, $\pm .0011$
Penny, 2d “.....	135.633, $\pm .0011$
Stas.....	135.6423, $\pm .0014$
Hibbs.....	135.627, $\pm .0026$
	<hr/>
General mean, .....	135.636, $\pm .0007$

By the same general process Penny† determined how much potassium nitrate could be formed from 100 parts of chlorate. He found as follows:

82.505
82.497
82.498
82.500
<hr/>
Mean, 82.500, $\pm .0012$

For 100 parts of sodium chlorate he found of nitrate:

79.875
79.882
79.890
<hr/>
Mean, 79.8823, $\pm .0029$

For the ratio between the chloride and nitrate of sodium Penny made two sets of estimations, as in the case of potassium salts. The subjoined figures give the amount of nitrate equivalent to 100 parts of chloride:

\* Thesis for Doctor's degree, University of Pennsylvania, 1896. Work done under the direction of Professor E. F. Smith.

† Phil. Trans., 1839.

*First Series.—NaCl treated with HNO<sub>3</sub>.*

145.415  
 145.408  
 145.420  
 145.424  
 145.410  
 145.418  
 145.420

Mean, 145.4164,  $\pm .0015$

*Second Series.—NaNO<sub>3</sub> treated with HCl.*

145.419  
 145.391  
 145.412  
 145.415  
 145.412  
 145.412

Mean, 145.410,  $\pm .0026$

Stas\* gives the following series:

145.453  
 145.468  
 145.465  
 145.469  
 145.443

Mean, after reducing to vacuum standard, 145.4526,  $\pm .0030$

Hibbs'† data, obtained by the method employed in the case of the potassium compounds, are as follows, vacuum weights being stated:

<i>Weight NaNO<sub>3</sub>.</i>	<i>Weight NaCl.</i>	<i>Ratio.</i>
.01550	.01066	145.403
.20976	.14426	145.404
.26229	.18038	145.410
.66645	.45829	145.429
.93718	.64456	145.399

Mean, 145.407,  $\pm .0026$

Combining, we have as follows:

Penny, 1st series. ....	145.4164, $\pm .0015$
Penny, 2d " ....	145.410, $\pm .0026$
Stas. ....	145.4526, $\pm .0030$
Hibbs. ....	145.407, $\pm .0026$
General mean. ....	145.418, $\pm .0012$

\* Aronstein's translation, p. 278.

† Thesis, University of Pennsylvania, 1896.



Julius Thomsen,\* for the purpose of fixing indirectly the ratio  $H : O$ , has made a valuable series of determinations of the ratio  $HCl : NH_3$ , which may properly be used toward establishing the atomic weight of nitrogen. First, pure, dry, gaseous hydrochloric acid is passed into a weighed absorption apparatus containing pure distilled water. After noting the increase in weight, pure ammonia gas is passed in until a very slight excess is present, and the apparatus is weighed again. The excess of  $NH_3$ , which is always minute, is measured by titration with standard hydrochloric acid. In weighing, the apparatus is tared by one of similar form, and containing about the same amount of water. Three series of determinations were made, differing only in the size of the absorption apparatus; so that for present purposes the three may be taken as one. Thomsen considers them separately, and so gives greatest weight to the experiments involving the largest masses of material. I give his weighings, and also, as computed by him, the ratio  $\frac{HCl}{NH_3}$ .

	<i>HCl.</i>	<i>NH<sub>3</sub>.</i>	<i>Ratio.</i>
First series. . . . .	5.1624	2.4120	2.1403
	3.9425	1.8409	2.1416
	4.6544	2.1739	2.1411
	3.9840	1.8609	2.1409
	5.3295	2.4898	2.1406
	4.2517	1.9863	2.1405
	4.8287	2.2550	2.1414
	6.4377	3.0068	2.1411
	4.1804	1.9528	2.1407
	5.0363	2.3523	2.1410
	4.6408	2.1685	2.1411
Second series. . . .	11.8418	5.5302	2.14130
	14.3018	6.6808	2.14073
	12.1502	5.6759	2.14067
	11.5443	5.3927	2.14073
	12.3617	5.7733	2.14118
Third series. . . . .	19.3455	9.0360	2.14094
	19.4578	9.0890	2.14081

Mean of all, 2.14093,  $\pm .000053$   
 Reduced to vacuo, 2.1394

From the sums of the weights Thomsen finds the ratio to be 2.14087, or 2.13934 in vacuo. From this, using Ostwald's reductions of Stas' data for the atomic weights of N and Cl, he finds the atomic weight of H = 0.99946, when O = 16.

We have now, apart from the determinations of gaseous density, eleven ratios, representing one hundred and sixty-four experiments, from which

\* Zeitsch. Physikal. Chem., 13, 398. 1894.

to calculate the atomic weight of nitrogen. Let us first collect and number these ratios :

- (1.)  $\text{Ag} : \text{AgNO}_3 :: 100 : 157.479, \pm .0003$
- (2.)  $\text{AgNO}_3 : \text{AgCl} :: 100 : 84.3743, \pm .0025$
- (3.)  $\text{AgNO}_3 : \text{KCl} :: 100 : 43.8715, \pm .0004$
- (4.)  $\text{AgNO}_3 : \text{NH}_4\text{Cl} :: 100 : 31.488, \pm .0006$
- (5.)  $\text{Ag} : \text{NH}_4\text{Cl} :: 100 : 49.5983, \pm .00031$
- (6.)  $\text{Ag} : \text{NH}_4\text{Br} :: 100 : 90.8299, \pm .0008$
- (7.)  $\text{KCl} : \text{KNO}_3 :: 100 : 135.636, \pm .0007$
- (8.)  $\text{KClO}_3 : \text{KNO}_3 :: 100 : 82.500, \pm .0012$
- (9.)  $\text{NaCl} : \text{NaNO}_3 :: 100 : 145.418, \pm .0011$
- (10.)  $\text{NaClO}_3 : \text{NaNO}_3 :: 100 : 79.8823, \pm .0029$
- (11.)  $\text{NH}_3 : \text{HCl} :: 1.00 : 2.1394, \pm .000053$

From these ratios we are now able to deduce the molecular weight of ammonium chloride, ammonium bromide, and three nitrates. For these calculations we must use the already ascertained atomic weights of oxygen, silver, chlorine, bromine, sodium and potassium, and the molecular weights of sodium chloride, potassium chloride, and silver chloride. The following are the antecedent values to be employed :

Ag	=	107.108, $\pm .0031$
K	=	38.817, $\pm .0051$
Na	=	22.881, $\pm .0046$
Cl	=	35.179, $\pm .0048$
Br	=	79.344, $\pm .0062$
O <sub>3</sub>	=	47.637, $\pm .0009$
AgCl	=	142.287, $\pm .0037$
KCl	=	74.025, $\pm .0019$
NaCl	=	58.060, $\pm .0017$

Now, from ratio number five we get the molecular weight of  $\text{NH}_4\text{Cl} = 53.124, \pm .0016$ , and  $\text{N} = 13.945, \pm .0051$ .

From ratio number six,  $\text{NH}_4\text{Br} = 97.286, \pm .0029$ , and  $\text{N} = 13.942, \pm .0077$ .

From ratio number eleven,  $\text{NH}_3 = 16.911, \pm .0048$ , and  $\text{N} = 13.911, \pm .0048$ .

From ratio number four, which involves an expression of the type  $\text{A} : \text{B} :: \text{C} + x : \text{D} + x$ , an independent value is deducible,  $\text{N} = 13.935, \pm .0073$ .

For the molecular weight of silver nitrate there are three values, namely :

From (1).....	$\text{AgNO}_3 = 168.673, \pm .0049$
From (2).....	" = 168.634, $\pm .0066$
From (3) .....	" = 168.731, $\pm .0046$
<hr/>	
General mean.....	$\text{AgNO}_3 = 168.690, \pm .0030$

Hence  $\text{N} = 13.945, \pm .0044$ .

The molecular weight of potassium nitrate is twice calculable, as follows :

From (7).....	$\text{KNO}_3 = 100.405, \pm .0026$
From (8).....	$\text{“} = 100.371, \pm .0059$
<hr/>	
General mean.....	$\text{KNO}_3 = 100.401, \pm .0024$

Hence  $N = 13.947, \pm .0057$ .

And for sodium nitrate we have :

From (9).....	$\text{NaNO}_3 = 84.430, \pm .0026$
From (10).....	$\text{“} = 84.433, \pm .0053$
<hr/>	
General mean.....	$\text{NaNO}_3 = 84.431, \pm .0023$

Hence  $N = 13.913, \pm .0052$ .

There are now seven estimates of the atomic weight of nitrogen, to be combined by means of the usual formula.

1. From $\text{NH}_4\text{Cl}$ .....	$N = 13.945, \pm .0051$
2. “ $\text{NH}_4\text{Br}$ .....	$\text{“} = 13.942, \pm .0077$
3. “ ratio (4).....	$\text{“} = 13.935, \pm .0073$
4. “ “ (11).....	$\text{“} = 13.911, \pm .0048$
5. “ $\text{AgNO}_3$ .....	$\text{“} = 13.945, \pm .0044$
6. “ $\text{KNO}_3$ .....	$\text{“} = 13.947, \pm .0057$
7. “ $\text{NaNO}_3$ .....	$\text{“} = 13.913, \pm .0052$
<hr/>	
General mean.....	$N = 13.935, \pm .0021$

If oxygen is 16, this becomes 14.041. From Stas' data alone, Stas finds 14.044; Ostwald, 14.0410; Van der Plaats, 14.0421 (A), and 14.0519 (B); and Thomsen, 14.0396. The new value, representing all available data, falls between these limits of variation.

## CARBON.

Although there is a large mass of material relating to the atomic weight of carbon, much of it may be summarily set aside as having no value for present purposes. The density of carbon dioxide, which has been scrupulously determined by many investigators,\* leads to no safe estimate of the constant under consideration. The numerous analyses of hydrocarbons, like the analyses of naphthalene by Mitscherlich, Woskresensky, Fownes, and Dumas, give results scarcely more satisfactory. In short, all the work done upon the atomic weight of carbon before the year 1840 may be safely rejected as unsuited to the present requirements of exact science. As for methods of estimation we need consider but four, as follows:

*First.* The analysis of organic salts of silver.

*Second.* The determination of the weight of carbon dioxide formed by the combustion of a known weight of carbon.

*Third.* The method of Stas, by the combustion of carbon monoxide.

*Fourth.* From the density of carbon monoxide.

The first of these methods, which is probably the least accurate, was employed by Liebig and Redtenbacher † in 1840. They worked with the acetate, tartrate, racemate, and malate of silver, making five ignitions of each salt, and determining the percentage of metal. From one to nine grammes of material were used in each experiment.

In the acetate the following percentages of silver were found:

64.615

64.624

64.623

64.614

64.610

Mean, 64.6172,  $\pm .0018$

After applying corrections for weighing in air, this mean becomes 64.6065.

In the tartrate the silver came out as follows:

59.297

59.299

59.287

59.293

59.293

Mean, 59.2938,  $\pm .0014$

Or, reduced to a vacuum, 59.2806

\* Notably by Lavoisier, Biot and Arago, De Saussure, Dulong and Berzelius, Buff, Von Wrede, Regnault, and Marchand. For details, Van Geun's monograph may be consulted.

† Ann. Chem. Pharm., 38, 137. Mem. Chem. Soc., 1, 9. Phil. Mag. (3), 19, 210.

In the racemate we have:

59.290
59.292
59.287
59.283
59.284
<hr/>
Mean, 59.2872, $\pm .0012$
Or, corrected, 59.2769

And from the malate:

61.996
61.972
62.015
62.059
62.011
<hr/>
Mean, 62.0106, $\pm .0096$
Or, corrected, 62.0016

Now, applying to these mean results the atomic weights already found for oxygen and silver, we get the following values for carbon:

From the acetate.....	C = 11.959, $\pm .0021$
From the tartrate .....	" = 11.967, $\pm .0019$
From the racemate.....	" = 11.973, $\pm .0017$
From the malate.....	" = 11.972, $\pm .0098$

Now these results, although remarkably concordant, are by no means unimpeachable. They involve two possible sources of constant error, namely, impurity of material and the volatility of the silver. These objections have both been raised by Stas, who found that the silver tartrate, prepared as Liebig and Redtenbacher prepared it, always carried traces of the nitrate, and that he, by the ignition of that salt, could not get results at all agreeing with theirs. In the case of the acetate a similar impurity would lower the percentage of silver, and thus both sources of error would reinforce each other and make the atomic weight of carbon come out too high. With the three other salts the two sources of error act in opposite directions, although the volatility of the silver is probably far greater in its influence than the impurity. Even if we had no other data relating to the atomic weight of carbon, it would be clear from these facts that the results obtained by Liebig and Redtenbacher must be decidedly in excess of the true figure.

Strecker,\* however, discussed the data given by Liebig and Redtenbacher by the method of least squares, using the Berzelian scale, and assuming  $H = 12.51$ . Thus treated, they gave  $C = 75.415$ , and  $Ag = 1348.79$ ; or, with  $O = 16$ ,  $C = 12.066$  and  $Ag = 107.903$ . These values

\* Ann. Chem. Pharm., 59, 280. 1846.

of course would change somewhat upon adoption of the modern ratio between O and H.

Observations upon silver acetate, like those of Liebig and Redtenbacher, were also made by Marignac.\* The salt was prepared by dissolving silver carbonate in acetic acid, and repeatedly recrystallizing. Two experiments gave as follows:

3.3359	gram. acetate gave	2.1561	Ag.	64.633	per cent.
3.0527	“	1.9727	“	64.621	“
				Mean, 64.627, $\pm .0040$	

Reduced to a vacuum, this becomes 64.609.

In a second series, conducted with special precautions to avoid mechanical loss by spurling, Marignac found:

24.717	gram. acetate gave	15.983	Ag.	64.665	per cent.
21.202	“	13.709	“	64.661	“
31.734	“	20.521	“	64.666	“
				<hr/>	
				Mean, 64.664, $\pm .0010$	
Or, reduced to a vacuum, 64.646					

Other experiments, comparable with the preceding series, have recently been published by Hardin,† who sought to redetermine the atomic weight of silver. Silver acetate and silver benzoate, carefully purified, were subjected to electrolysis in a platinum dish, and the percentage of silver so determined. For the acetate, using vacuum weights, he gives the following data, the percentage column being added by myself:

.32470	gram. acetate gave	.20987	Ag.	64.635	per cent.
.40566	“	.26223	“	64.643	“
.52736	“	.34086	“	64.635	“
.60300	“	.38976	“	64.637	“
.67235	“	.43455	“	64.631	“
.72452	“	.46830	“	64.636	“
.78232	“	.50563	“	64.632	“
.79804	“	.51590	“	64.646	“
.92101	“	.59532	“	64.638	“
1.02495	“	.66250	“	64.637	“
				Mean, 64.637, $\pm .0011$	

Combining this series with those of the earlier investigators we have:

Liebig and Redtenbacher.....	64.6065, $\pm .0018$
Marignac, 1st series.....	64.609, $\pm .0040$
Marignac, 2d “.....	64.646, $\pm .0010$
Hardin.....	64.637, $\pm .0011$
General mean.....	64.636, $\pm .0007$

\* Ann. Chem. Pharm., 59, 287. 1846.

† Journ. Amer. Chem. Soc., 18, 990. 1896.

With silver benzoate,  $C_7H_5AgO_2$ , Hardin's results are as follows :

.40858	gram. benzoate gave	.19255	Ag.	47.127	per cent.
.46674	"	.21999	"	47.133	"
.48419	"	.22815	"	47.120	"
.62432	"	.29418	"	47.120	"
.66496	"	.31340	"	47.131	"
.75853	"	.35745	"	47.124	"
.76918	"	.36247	"	47.124	"
.81254	"	.38286	"	47.119	"
.95673	"	.45079	"	47.118	"
1.00840	"	.47526	"	47.130	"

Mean, 47.125,  $\pm .0012$

A different method of dealing with organic silver salts was adopted by Maumené,\* in 1846, for the purpose of establishing by reference to carbon the atomic weight of silver. We will simply reverse his results and apply them to the atomic weight of carbon. He effected the combustion of the acetate and the oxalate of silver, and, by weighing both the residual metal and the carbon dioxide formed, he fixed the ratio between these two substances. In the case of the acetate his weighings show that for every gramme of metallic silver the weights of  $CO_2$  were produced which are shown in the third column :

8.083	gram. Ag =	6.585	gram. $CO_2$ .	.8147
11.215	"	9.135	"	.8136
14.351	"	11.6935	"	.8148
9.030	"	7.358	"	.8148
20.227	"	16.475	"	.8145

Mean, .81448

The oxalate of silver, ignited by itself, decomposes too violently to give good results ; and for this reason it was not used by Liebig and Redtenbacher. Maumené, however, found that when the salt was mixed with sand the combustion could be tranquilly effected. The oxalate employed, however, with the exception of the sample represented in the last experiment of the series, contained traces of nitrate, so that these results involve slight errors. For each gramme of silver the appended weights of  $CO_2$  were obtained :

14.299	gram. Ag. =	5.835	gram. $CO_2$ .	.4081
17.754	"	7.217	"	.4059
11.550	"	4.703	"	.4072
10.771	"	4.387	"	.4073
8.674	"	3.533	"	.4073
11.4355	"	4.658	"	.4073

Mean, .40718

\*Ann. Chim. Phys. (3), 18, 41. 1846.

Now, one of these salts being formed by a bivalent and the other by a univalent acid, we have to reduce both to a common standard. Doing this, we have the following results for the ratio between the atomic weight of silver and the molecular weight of  $\text{CO}_2$ ; if  $\text{Ag} = 1.00$ :

From the acetate.....	$\text{CO}_2 = .40724, \pm .000076$
From the oxalate.....	" = $.40718, \pm .000185$
General mean.....	$\text{CO}_2 = .40723, \pm .000071$

Here the slight error due to the impurity of the oxalate becomes of such trifling weight that it practically vanishes.

As has already been said, the volatility of silver renders all the foregoing results more or less uncertain. Far better figures are furnished by the combustion of carbon directly, as carried out by Dumas and Stas\* in 1840 and by Erdmann and Marchand† in 1841. In both investigations weighed quantities of diamond, of natural graphite, and of artificial graphite were burned in oxygen, and the amount of dioxide produced was estimated by the usual methods. The graphite employed was purified with extreme care by treatment with strong nitric acid and by fusion with caustic alkali. I have reduced all the published weighings to a common standard, so as to show in the third column the amount of oxygen which combines with a unit weight (say one gramme) of carbon. Taking Dumas and Stas' results first in order, we have from natural graphite:

1.000 grm. C gave	3.671 grm. $\text{CO}_2$ .	2.6710
.998	" 3.660 "	2.6673
.994	" 3.645 "	2.6670
1.216	" 4.461 "	2.6686
1.471	" 5.395 "	2.6676
		<hr/>
		Mean, 2.6683, $\pm .0005$

With artificial graphite:

.992 grm. C gave	3.642 grm. $\text{CO}_2$ .	2.6714
.998	" 3.662 "	2.6682
1.660	" 6.085 "	2.6654
1.465	" 5.365 "	2.6744
		<hr/>
		Mean, 2.66985, $\pm .0013$

And with diamond:

.708 grm. C gave	2.598 grm. $\text{CO}_2$ .	2.6695
.864	" 3.1675 "	2.6661
1.219	" 4.465 "	2.6628
1.232	" 4.519 "	2.6680
1.375	" 5.041 "	2.6662
		<hr/>
		Mean, 2.6665 $\pm .0007$

\* Compt. Rend., 11, 991-1008. Ann. Chim. Phys. (3), 1, 1.

† Jour. f. Prakt. Chem., 23, 159.



Erdmann and Marchand's figures for natural graphite give the following results :

1.5376	gram.	gave	5.6367	gram.	CO <sub>2</sub> .	2.6659
1.6494	"		6.0384	"	"	2.6609
1.4505	"		5.31575	"	"	2.6647

In one experiment 1.8935 gram. of artificial graphite gave 6.9355 gram. CO<sub>2</sub>. Ratio for O, 2.6628. This, combined with the foregoing series, gives a mean of 2.6636,  $\pm .0007$ .

With the diamond they found :

.8052	gram.	gave	2.9467	gram.	CO <sub>2</sub> .	2.6596
1.0858	"		3.9875	"	"	2.6632
1.3557	"		4.9659	"	"	2.6629
1.6305	"		5.97945	"	"	2.6673
.7500	"		2.7490	"	"	2.6653

Mean, 2.6637,  $\pm .0009$

In more recent years the ratio under consideration has been carefully redetermined by Roscoe, by Friedel, and by Van der Plaats. Roscoe\* made use of transparent Cape diamonds, and in a sixth experiment he burned carbonado. The combustions were effected in a platinum boat, contained in a tube of glazed Berlin porcelain; and in each case the ash was weighed and its weight deducted from that of the diamond. The results were as follows, with the ratios stated as in the preceding series :

1.2820	gram.	C gave	4.7006	CO <sub>2</sub> .	2.6666
1.1254	"		4.1245	"	2.6649
1.5287	"		5.6050	"	2.6665
.7112	"		2.6070	"	2.6656
1.3842	"		5.0765	"	2.6675
.4091	"		1.4978	"	2.6612

Mean, 2.6654,  $\pm .0006$

Friedel's work,† also upon Cape diamond, was in all essential particulars like Roscoe's. The data, after deduction of ash, were as follows :

.4705	gram.	C gave	1.7208	CO <sub>2</sub> .	2.6628
.8616	"		3.1577	"	2.6640

Mean, 2.6634,  $\pm .0004$

By Van der Plaats‡ we have six experiments, numbers one to three on graphite, numbers four and five on sugar charcoal, and number six on charcoal made from purified filter paper. Each variety of carbon was submitted to elaborate processes of purification, and all weights were

\* Ann. Chim. Phys. (5), 26, 136. Zeit. Anal. Chem., 22, 306. 1883. Compt. Rend., 94, 1180. 1882.

† Bull. Soc. Chim., 42, 100, 1884.

‡ Compt. Rend., 100, 52. 1885.

reduced to vacuum standards. The data, with ash deducted, are subjoined:

1.	5.1217	gm. C gave	18.7780	CO <sub>2</sub> .	2.6664
2.	9.0532	"	33.1931	"	2.6664
3.	13.0285	"	47.7661	"	2.6663
4.	11.7352	"	43.0210	"	2.6660
5.	19.1335	"	70.1336	"	2.6655
6.	4.4017	"	16.1352	"	2.6657

Mean, 2.6660,  $\pm .0001$

This combines with the previous series thus:

Dumas and Stas, first set.....	2.6683, $\pm .0005$
Dumas and Stas, second set.....	2.66985, $\pm .0013$
Dumas and Stas, third set.....	2.6665, $\pm .0007$
Erdmann and Marchand, first set.....	2.6636, $\pm .0007$
Erdmann and Marchand, second set.....	2.6637, $\pm .0009$
Roscoe.....	2.6654, $\pm .0006$
Friedel.....	2.6634, $\pm .0004$
Van der Plaats.....	2.6660, $\pm .0001$

General mean.... 2.6659,  $\pm .0001$

Another very exact method for determining the atomic weight of carbon was employed by Stas\* in 1849. Carefully purified carbon monoxide was passed over a known weight of copper oxide at a red heat, and both the residual metal and the carbon dioxide formed were weighed. The weighings were reduced to a vacuum standard, and in each experiment a quantity of copper oxide was taken representing from eight to twenty-four grammes of oxygen. The method, as will at once be seen, is in all essential features similar to that usually employed for determining the composition of water. The figures in the third column, deduced from the weights given by Stas, represent the quantity of carbon monoxide corresponding to one gramme of oxygen:

9.265	gm. O =	25.483	CO <sub>2</sub> .	1.75046
8.327	"	22.900	"	1.75010
13.9438	"	38.351	"	1.75040
11.6124	"	31.935	"	1.75008
18.763	"	51.6055	"	1.75039
19.581	"	53.8465	"	1.74994
22.515	"	61.926	"	1.75043
24.360	"	67.003	"	1.75053

Mean, 1.75029,  $\pm .00005$

For the density of carbon monoxide the determinations made by Leduc† are available. The globe used contained 2.9440 gm. of air.

\* Bull. Acad. Bruxelles, 1849 (1), 31.

† Compt. Rend., 115, 1072. 1893.

Filled with CO, it held the following weights, which give the accompanying densities:

<i>Wt. CO.</i>	<i>Density.</i>
2.8470	.96705
2.8468	.96698
2.8469	.96702
<hr/>	
Mean, .96702, $\pm$ .000015	

Combining this density with Ledue's determination of the density of hydrogen, 0.6948,  $\pm$  .00006745, it gives for the atomic weight of carbon:

$$C = 11.957, \pm .0270.$$

Ledue himself combines the data with the density of oxygen, taken as 1.10503, and finds  $C = 11.913$ . In either case, however, the probable error of the result is so high that it can carry little weight in the final combination.

For carbon, including all the foregoing series, we now have the subjoined ratios:

- (1.) Per cent. Ag in silver acetate. . . . 64.636,  $\pm$  .0007
- (2.) " " tartrate. . . . 59.2806,  $\pm$  .0014
- (3.) " " racemate. . . . 59.2769,  $\pm$  .0012
- (4.) " " malate . . . . 62.0016,  $\pm$  .0096
- (5.) " " benzoate. . . . 47.125,  $\pm$  .0012
- (6.) Ag : CO<sub>2</sub> : : 1.00 : 0.40723,  $\pm$  .000071
- (7.) C : O<sub>2</sub> : : 1.00 : 2.6659,  $\pm$  .0001
- (8.) O : CO : : 1.00 : 1.75029,  $\pm$  .00005
- (9.) Density of CO (air = 1), 0.96702,  $\pm$  .000015

Now, computing with O = 15.879,  $\pm$  .0003, and Ag = 107.108,  $\pm$  .0031, we get nine values for the atomic weight of carbon, as follows:

From (1).....	C = 11.921, $\pm$ .0012
From (2).....	" = 11.967, $\pm$ .0019
From (3).....	" = 11.973, $\pm$ .0017
From (4).....	" = 11.972, $\pm$ .0098
From (5).....	" = 11.917, $\pm$ .0008
From (6).....	" = 11.860, $\pm$ .0077
From (7).....	" = 11.913, $\pm$ .0006
From (8).....	" = 11.914, $\pm$ .0010
From (9).....	" = 11.957, $\pm$ .0270
<hr/>	
General mean.....	C = 11.920, $\pm$ .0004

If O = 16, this becomes  $C = 12.011$ .

## SULPHUR.

The atomic weight of sulphur has been determined by means of four ratios connecting it with silver, chlorine, oxygen, sodium and carbon. Other ratios have also been considered, but they are hardly applicable here. The earlier results of Berzelius were wholly inaccurate, and his later experiments upon the synthesis of lead sulphate will be used in discussing the atomic weight of lead. Erdmann and Marchand determined the amount of calcium sulphate which could be formed from a known weight of pure Iceland spar; and later they made analyses of cinnabar, in order to fix the value of sulphur by reference to calcium and to mercury. Their results will be applied in this discussion toward ascertaining the atomic weights of the metals just named.

First in order let us take up the composition of silver sulphide, as directly determined by Dumas, Stas, and Cooke. Dumas'\* experiments were made with sulphur which had been thrice distilled and twice crystallized from carbon disulphide. A known weight of silver was heated in a tube in the vapor of the sulphur, the excess of the latter was distilled away in a current of carbon dioxide, and the resulting silver sulphide was weighed.

I subjoin Dumas' weighings, and also the quantity of  $\text{Ag}_2\text{S}$  proportional to 100 parts of Ag, as deduced from them:

9.9393	grm.	Ag = 1.473	S.	Ratio, 114.820
9.962	"	1.4755	"	" 114.811
30.637	"	4.546	"	" 114.838
30.936	"	4.586	"	" 114.824
30.720	"	4.554	"	" 114.824
				<hr/>
				Mean, 114.8234, $\pm .0029$

Dumas used from ten to thirty grammes of silver in each experiment. Stas, † however, in his work employed from sixty to two hundred and fifty grammes at a time. Three of Stas' determinations were made by Dumas' method, while in the other two the sulphur was replaced by pure sulphuretted hydrogen. In all cases the excess of sulphur was expelled by carbon dioxide, purified with scrupulous care. Impurities in the dioxide may cause serious error. The five results come out as follows for 100 parts of silver:

114.854
114.853
114.854
114.851
114.849
<hr/>

Mean, 114.8522,  $\pm .0007$

\* Ann. Chem. Pharm., 113, 24. 1860.

† Aronstein's translation, p. 179.

The experiments made by Professor Cooke\* with reference to this ratio were only incidental to his elaborate researches upon the atomic weight of antimony. They are interesting, however, for two reasons: they serve to illustrate the volatility of silver, and they represent, not syntheses, but reductions of the sulphide by hydrogen. Cooke gives three series of results. In the first the silver sulphide was long heated to full redness in a current of hydrogen. Highly concordant and at the same time plainly erroneous figures were obtained, the error being eventually traced to the fact that some of the reduced silver, although not heated to its melting point, was actually volatilized and lost. The second series, from reductions at low redness, are decidedly better. In the third series the sulphide was fully reduced below a visible red heat. Rejecting the first series, we have from Cooke's figures in the other two the subjoined quantities of sulphide corresponding to 100 parts of silver:

7.5411 grm. $\text{Ag}_2\text{S}$ lost .9773 grm. S.	Ratio, 114.889
5.0364       "       .6524       "	"   114.882
2.5815       "       .3345       "	"   114.886
2.6130       "       .3387       "	"   114.892
2.5724       "       .3334       "	"   114.891
<hr/>	
Mean, 114.888, $\pm .0012$	
1.1357 grm. $\text{Ag}_2\text{S}$ lost .1465 S.	Ratio, 114.810
1.2936       "       .1670       "	"   114.823
<hr/>	
Mean, 114.8165, $\pm .0044$	

Now, combining all four series, we get the following results:

Dumas.....	114.8234, $\pm .0029$
Stas.....	114.8522, $\pm .0007$
Cooke's 2d.....	114.888, $\pm .0012$
Cooke's 3d.....	114.8165, $\pm .0044$
<hr/>	
General mean.....	114.8551, $\pm .0006$

Here again we encounter a curious and instructive compensation of errors, and another evidence of the accuracy of Stas.

The percentage of silver in silver sulphate has been determined by Struve and by Stas. Struve† reduced the sulphate by heating in a current of hydrogen, and obtained these results:

5.1860 grm. $\text{Ag}_2\text{SO}_4$ gave 3.5910 grm. Ag.	69.244 per cent.
6.0543       "       4.1922       "	69.243       "
8.6465       "       5.9858       "	69.228       "
11.6460       "       8.0608       "	69.215       "
9.1090       "       6.3045       "	69.212       "
9.0669       "       6.2778       "	69.239       "
<hr/>	
Mean, 69.230, $\pm .004$	

\* Proc. Amer. Acad. of Arts and Sciences, vol. 12. 1877.

† Ann. Chem. Pharm., 50, 203. 1851.

Stas,\* working by essentially the same method, with from 56 to 83 grammes of sulphate at a time, found these percentages :

69.200  
69.197  
69.204  
69.209  
69.207  
69.202

Mean, 69.203,  $\pm .0012$

Combining this mean with that from Struve's series, we get a general mean of 69.205,  $\pm .0011$ .

The third sulphur ratio with which we have now to deal is one of minor importance. When silver chloride is heated in a current of sulphuretted hydrogen the sulphide is formed. This reaction was applied by Berzelius† to determining the atomic weight of sulphur. He gives the results of four experiments; but the fourth varies so widely from the others that I have rejected it. I have reason to believe that the variation is due, not to error in experiment, but to error in printing; nevertheless, as I am unable to track out the cause of the mistake, I must exclude the figures involving it entirely from our discussion.

The three available experiments, however, give the following results: The last column contains the ratio of silver sulphide to 100 parts of chloride.

6.6075	gm. AgCl gave	5.715	gm. Ag <sub>2</sub> S.	86.478
9.2323	"	7.98325	"	86.471
10.1775	"	8.80075	"	86.472

Mean, 86.4737,  $\pm .0015$

We have also a single determination of this value by Svanberg and Struve.‡ After converting the chloride into sulphide they dissolved the latter in nitric acid. A trifling residue of chloride, which had been enclosed in sulphide, and so protected against change, was left undissolved. Hence a slight constant error probably affects this whole ratio. The experiment of Svanberg and Struve gave 86.472 per cent. of silver sulphide derived from 100 of chloride. If we assign this figure equal weight with the results of Berzelius, and combine, we get a general mean of 86.4733,  $\pm .0011$ .

The work done by Richards§ relative to the atomic weight of sulphur is of a different order from any of the preceding determinations. Sodium carbonate was converted into sodium sulphate, fixing the ratio Na<sub>2</sub>CO<sub>3</sub> : Na<sub>2</sub>SO<sub>4</sub> : : 100 : x. The data are as follows, with vacuum weights :

\* Aronstein's translation, pp. 214-218.

† Berzelius' Lehrbuch, 5th ed., vol. 3, p. 1187.

‡ Journ. Prakt. Chem., 44, 320. 1845.

§ Proc. Amer. Acad., 26, 268. 1891.

$Na_2CO_3$ .	$Na_2SO_4$ .	<i>Ratio.</i>
1.29930	1.74113	134.005
3.18620	4.26790	133.950
1.01750	1.36330	133.985
2.07680	2.78260	133.985
1.22427	1.63994	133.952
1.77953	2.38465	134.005
2.04412	2.73920	134.004
3.06140	4.10220	133.997

Mean, 133.985,  $\pm .0055$

The available ratios for sulphur are now as follows:

- (1.)  $Ag_2 : Ag_2S :: 100 : 114.8581, \pm .0006$
- (2.) Per cent. Ag in  $Ag_2SO_4$ , 69.205,  $\pm .0011$
- (3.)  $2 AgCl : Ag_2S :: 100 : 86.4733, \pm .0011$
- (4.)  $Na_2CO_3 : Na_2SO_4 :: 100 : 133.985, \pm .0055$

From these ratios, four values for the atomic weight of sulphur are deducible. Calculating with—

$$\begin{aligned}
 O &= 15.879, \pm .0003 \\
 Ag &= 107.108, \pm .0031 \\
 Cl &= 35.179, \pm .0048 \\
 Na &= 22.881, \pm .0046 \\
 C &= 11.920, \pm .0004 \\
 AgCl &= 142.287, \pm .0037,
 \end{aligned}$$

we have:

$$\begin{aligned}
 \text{From (1) } &\dots\dots\dots S = 31.828, \pm .0016 \\
 \text{From (2) } &\dots\dots\dots " = 31.806, \pm .0048 \\
 \text{From (3) } &\dots\dots\dots " = 31.864, \pm .0086 \\
 \text{From (4) } &\dots\dots\dots " = 31.835, \pm .0191 \\
 \text{General mean } &\dots\dots\dots S = 31.828, \pm .0015
 \end{aligned}$$

If  $O = 16$ ,  $S = 32.070$ . From Stas' ratios alone, Stas found 32.074; Ostwald, 32.0626; Van der Plaats, (A) 32.0576, (B) 32.0590, and Thomsen, 32.0606. Here again Stas' determinations far outweigh all others.

## LITHIUM.

The earlier determinations of the atomic weight of lithium by Arfvedson, Stromeyer, C. G. Gmelin, and Kralovanzky were all erroneous, because of the presence of sodium compounds in the material employed. The results of Berzelius, Hagen, and Hermann were also incorrect, and need no further notice here. The only investigations which we need to consider are those of Mallet, Diehl, Troost, Stas, and Dittmar.

Mallet's experiments\* were conducted upon lithium chloride, which had been purified as completely as possible. In two trials the chloride was precipitated by nitrate of silver, which was collected upon a filter and estimated in the ordinary way. The figures in the third column represent the LiCl proportional to 100 parts of AgCl:

7.1885	gm. LiCl gave	24.3086	gm. AgCl.	29.606
8.5947	“	29.0621	“	29.574

In a third experiment the LiCl was titrated with a standard solution of silver. 3.9942 gm. LiCl balanced 10.1702 gm. Ag, equivalent to 13.511 gm. AgCl. Hence  $100 \text{ AgCl} = 29.563 \text{ LiCl}$ . Mean of all three experiments,  $29.581, \pm .0087$ .

Diehl,† whose paper begins with a good résumé of all the earlier determinations, describes experiments made with lithium carbonate. This salt, which was spectroscopically pure, was dried at  $130^\circ$  before weighing. It was then placed in an apparatus from which the carbon dioxide generated by the action of pure sulphuric acid upon it could be expelled, and the loss of weight determined. From this loss the following percentages of  $\text{CO}_2$  in  $\text{Li}_2\text{CO}_3$  were determined:

59.422
59.404
59.440
59.401
<hr/>
Mean, 59.417, $\pm .006$

Diehl's investigation was quickly followed by a confirmation from Troost.‡ This chemist, in an earlier paper,§ had sought to fix the atomic weight of lithium by an analysis of the sulphate, and had found a value not far from 6.5, thus confirming the results of Berzelius and of Hagen, who had employed the same method. But Diehl showed that the  $\text{BaSO}_4$  precipitated from  $\text{Li}_2\text{SO}_4$  always retained traces of Li, which were recog-

\* Silliman's Amer. Journal, November, 1856. Chem. Gazette, 15, 7.

† Ann. Chem. Pharm., 121, 93.

‡ Zeit. Anal. Chem., 1, 402.

§ Annales d. Chim. et d. Phys., 51, 105.



nizable by spectral analysis, and which accounted for the error. In the later paper Troost made use of the chloride and the carbonate of lithium, both spectroscopically pure. The carbonate was strongly ignited with pure quartz powder, thus losing carbon dioxide, which loss was easily estimated. The subjoined results were obtained:

.970	gram.	$\text{Li}_2\text{CO}_3$	lost	.577	gram.	$\text{CO}_2$ .	59.485	per cent.
1.782		"		1.059		"	59.427	"
							<u>Mean, 59.456, <math>\pm</math> .020</u>	

The lithium chloride employed by Troost was heated in a stream of dry hydrochloric acid gas, of which the excess, after cooling, was expelled by a current of dry air. The salt was weighed in the same tube in which the foregoing operations had been performed, and the chlorine was then estimated as silver chloride. The usual ratio between  $\text{LiCl}$  and 100 parts of  $\text{AgCl}$  is given in the third column:

1.309	gram.	$\text{LiCl}$	gave	4.420	gram.	$\text{AgCl}$ .	29 615
2.750		"		9.300		"	29.570
							<u>Mean, 29.5925, <math>\pm</math> .0145</u>

This, combined with Mallet's mean, 29.581,  $\pm$  .0087, gives a general mean of 29.584,  $\pm$  .0075.

Next in order is the work of Stas,\* which was executed with his usual wonderful accuracy. In three titrations, in which all the weights were reduced to a vacuum standard, the following quantities of  $\text{LiCl}$  balanced 100 parts of pure silver:

39.356
39.357
39.361
<u>Mean, 39.358, <math>\pm</math> .001</u>

In a second series of experiments, intended for determining the atomic weight of nitrogen,  $\text{LiCl}$  was converted into  $\text{LiNO}_3$ . The method was that employed for a similar purpose with the chlorides of sodium and of potassium. One hundred parts of  $\text{LiCl}$  gave of  $\text{LiNO}_3$ :

162.588
162 600
162.598
<u>Mean, 162.5953, <math>\pm</math> .0025</u>

The determinations of Dittmar† resemble those of Diehl; but the lithium carbonate used was dehydrated by fusion in an atmosphere of carbon dioxide. The carbonate was treated with sulphuric acid, and

\* Aronstein's translation, 279-302.

† Trans. Roy. Soc. Edinburgh, 35, II, 429. 1889.

the  $\text{CO}_2$  was collected and weighed in an absorption apparatus, which was tared by a similar apparatus after the method of Regnault. The following percentages of  $\text{CO}_2$  in  $\text{Li}_2\text{CO}_3$  were found :

59.601
59.645
59.529—rejected.
59.655
59.683
59.604
59.517
59.663
60.143—rejected.
59.794
59.584
<hr/>
Mean of all, 59.674

Rejecting the two experiments which Dittmar regards as untrustworthy, the mean of the remaining nine becomes  $59.638, \pm .0173$ . This combines with the work of Diehl and Troost, as follows :

Diehl.....	59.417, $\pm .0060$
Troost.....	59.456, $\pm .0200$
Dittmar.....	59.638, $\pm .0173$
	<hr/>
General mean.....	59.442, $\pm .0054$

Dittmar's determinations give a much lower value for the atomic weight of lithium than any of the others, and therefore seem to be questionable. As, however, they carry little weight in the general combination, it is not necessary to speculate upon their possible sources of error.

The ratios for lithium are now as follows :

- (1.)  $\text{AgCl} : \text{LiCl} :: 100 : 29.584, \pm .0075$
- (2.)  $\text{Ag} : \text{LiCl} :: 100 : 39.358, \pm .001.$
- (3.)  $\text{LiCl} : \text{LiNO}_3 :: 100 : 162.5953, \pm .0025$
- (4.) Per cent. of  $\text{CO}_2$  in  $\text{Li}_2\text{CO}_3$ ,  $59.442, \pm .0054$

And the data to use in their reduction are—

O = 15.879, $\pm .0003$	N = 13.935, $\pm .0015$
Ag = 107.108, $\pm .0031$	C = 11.920, $\pm .0004$
Cl = 35.179, $\pm .0048$	AgCl = 142.287, $\pm .0037$

These factors give two values for the molecular weight of lithium chloride, thus :

From (1).....	LiCl = 42.0942, $\pm .0110$
From (2).....	" = 42.1556, $\pm .0016$
	<hr/>
General mean.....	LiCl = 42.1542, $\pm .0016$

For lithium itself there are three values :

From molecular weight LiCl, . . . . .	Li = 6.9752, $\pm$ .0051
From (3), . . . . .	" = 6.9855, $\pm$ .0129
From (4), . . . . .	" = 6.9628, $\pm$ .0077
<hr/>	
General mean, . . . . .	Li = 6.9729, $\pm$ .0040

If O = 16, Li = 7.026. From Stas' ratios, Stas found Li = 7.022; Ostwald, 7.0303; Van der Plaats (A), 7.0273; (B), 7.0235; and Thomsen, 7.0307.

## RUBIDIUM.

The atomic weight of rubidium has been determined by Bunsen, Piccard, Godeffroy, and Heycock from analyses of the chloride and bromide.

Bunsen,\* employing ordinary gravimetric methods, estimated the ratio between AgCl and RbCl. His rubidium chloride was purified by fractional crystallization of the chloroplatinate. He obtained the following results, to which, in a third column, I add the ratio between RbCl and 100 parts of AgCl:

One gram, RbCl gave 1.1873 gram, AgCl,	84.225
" 1.1873 "	84.225
" 1.1850 "	84.388
" 1.1880 "	84.175
<hr/>	
Mean, 84.253, $\pm$ .031	

The work of Piccard† was similar to that of Bunsen. In weighing, the crucible containing the silver chloride was balanced by a precisely similar crucible, in order to avoid the correction for displacement of air. The filter was burned separately from the AgCl, as usual; but the small amount of material adhering to the ash was reckoned as metallic silver. The rubidium chloride was purified by Bunsen's method. The results, expressed according to the foregoing standard, are as follows:

1.1587 gram, RbCl = 1.372 AgCl + .0019 Ag.	84.300
1.4055 " 1.6632 " .0030 "	84.303
1.001 " 1.1850 " .0024 "	84.245
1.5141 " 1.7934 " .0018 "	84.313
<hr/>	
Mean, 84.290, $\pm$ .0105	

Godeffroy,‡ starting with material containing both rubidium and

\* Zeit. Anal. Chem., 1, 136. Poggend. Annal., 113, 339. 1861.

† Journ. für Prakt. Chem., 86, 474. 1862. Zeit. Anal. Chem., 1, 518.

‡ Ann. Chem. Pharm., 181, 185. 1876.

caesium, separated the two metals by fractional crystallization of their alums, and obtained salts of each spectroscopically pure. The nitric acid employed was tested for chlorine and found to be free from that impurity, and the weights used were especially verified. In two of his analyses of RbCl the AgCl was handled by the ordinary process of filtration. In the other two it was washed by decantation, dried, and weighed in a glass dish. The usual ratio is appended in the third column :

1.4055	gram. RbCl	gave	1.6665	gram. AgCl.	84.338
1.8096	"		2.1461	"	84.320
2.2473	"		2.665	"	84.326
2.273	"		2.6946	"	84.354
					<hr/>
					Mean, 84.3345, $\pm .0051$

Combining the three series, we get the following result :

Bunsen	.....	84.253, $\pm .031$	Rb = 84.702
Piccard	.....	84.290, $\pm .0105$	" = 84.754
Godeffroy	.....	84.3345, $\pm .0051$	" = 84.817
		<hr/>	
General mean.....		84.324, $\pm .0045$	

Heycock\* worked by two methods, but unfortunately his results are given only in abstract, without details. First, silver solution was added in slight deficiency to a solution of rubidium chloride, and the excess of the latter was measured by titration. The mean of seven experiments gave—

$$\text{Ag} : \text{RbCl} :: 107.93 : 120.801$$

Hence Rb = 84.702.

Two similar experiments with the bromide gave—

$$\begin{aligned} \text{Ag} : \text{RbBr} &:: 107.93 : 165.437 \\ \text{Ag} : \text{RbBr} &:: 107.93 : 165.342 \\ \hline \text{Mean, } &165.3895, \pm .0320 \end{aligned}$$

There are now three ratios for the metal rubidium, as follows :

- (1.)  $\text{AgCl} : \text{RbCl} :: 100 : 84.324, \pm .0045$
- (2.)  $\text{Ag} : \text{RbCl} :: 107.93 : 120.801$
- (3.)  $\text{Ag} : \text{RbBr} :: 107.93 : 165.3895, \pm .0320$

To reduce these ratios we have—

$$\begin{aligned} \text{Ag} &= 107.108, \pm .0031 \\ \text{Br} &= 79.344, \pm .0062 \\ \text{Cl} &= 35.179, \pm .0048 \\ \text{AgCl} &= 142.287, \pm .0037 \end{aligned}$$

---

\* British Association Report, 1882, p. 499.

For the molecular weight of  $\text{RbCl}$ , two values are calculable:

From (1).....	$\text{RbCl} = 119.981, \pm .0109$
From (2).....	" = $119.881, \pm .0218$
<hr/>	
General mean.....	$\text{RbCl} = 119.961, \pm .0097$

To the value from ratio (2) I have arbitrarily assigned a weight represented by the probable error as written above. The data for systematic weighting are deficient, and no other course of procedure seemed advisable.

From $\text{RbCl}$ .....	$\text{Rb} = 84.782, \pm .0109$
From $\text{RbBr}$ , ratio (3) .....	" = $84.786, \pm .0329$
<hr/>	
General mean.....	$\text{Rb} = 84.783, \pm .0103$

If  $\text{O} = 16$ ,  $\text{Rb} = 85.429$ .

## CÆSIUM.

The atomic weight of caesium, like that of rubidium, has been determined from the analysis of the chloride. The earliest determination, by Bunsen,\* was incorrect, because of impurity in the material employed.

In 1863 Johnson and Allen published their results.† Their material was extracted from the lepidolite of Hebron, Maine, and the caesium was separated from the rubidium as bitartrate. From the pure caesium bitartrate caesium chloride was prepared, and in this the chlorine was estimated as silver chloride by the usual gravimetric method. Reducing their results to the convenient standard adopted in preceding chapters, we have, in a third column, the quantities of  $\text{CsCl}$  equivalent to 100 parts of  $\text{AgCl}$ :

1.8371	gram. $\text{CsCl}$ gave	1.5634	gram. $\text{AgCl}$ .	117.507
2.1295	"	1.8111	"	117.580
2.7018	"	2.2992	"	117.511
1.56165	"	1.3302	"	117.399

Mean,  $117.499, \pm .025$

Shortly after the results of Johnson and Allen appeared a new series of estimations was published by Bunsen.‡ His caesium chloride was purified by repeated crystallizations of the chloroplatinate, and the ordi-

\* Zeit. Anal. Chem., 1, 137.

† Amer. Journ. Sci. and Arts (2), 35, 94.

‡ Poggend. Annalen, 119, 1. 1863.

nary gravimetric process was employed. The following results represent, respectively, material thrice, four times, and five times purified :

1.3835	gram.	CsCl gave	1.1781	gram.	AgCl.	Ratio,	117.435
1.3682		"	1.1644		"	"	117.503
1.2478		"	1.0623		"	"	117.462
							<hr/>
							Mean, 117.467, $\pm .013$

Godeffroy's work\* was, in its details of manipulation, sufficiently described under rubidium. In three of the experiments upon cesium the silver chloride was washed by decantation, and in one it was collected upon a filter. The results are subjoined :

1.5825	gram.	CsCl gave	1.351	gram.	AgCl.	Ratio,	117.135
1.3487		"	1.1501		"	"	117.265
1.1880		"	1.0141		"	"	117.148
1.2309		"	1.051		"	"	117.107
							<hr/>
							Mean, 117.164, $\pm .023$

We may now combine the three series to form a general mean :

Johnson and Allen . . . .	117.499, $\pm .025$	Cs = 132.007
Bunsen . . . . .	117.467, $\pm .013$	" = 131.961
Godeffroy . . . . .	117.164, $\pm .023$	" = 131.560
		<hr/>
General mean . . .	117.413, $\pm .010$	

Hence, if  $\text{AgCl} = 142.287, \pm .0037$ , and  $\text{Cl} = 35.179, \pm .0048$ ,  $\text{Cs} = 131.885, \pm .0142$ .

If  $\text{O} = 16$ ,  $\text{Cs} = 132.890$ .

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\* Ann. Chem. Pharm., 181, 185. 1876.

## COPPER.

The atomic weight of copper has been chiefly determined by means of the oxide, the sulphate, and the bromide, and by direct comparison of the metal with silver.

In dealing with the first-named compound all experimenters have agreed in reducing it with a current of hydrogen, and weighing the metal thus set free.

The earliest experiments of any value were those of Berzelius,\* whose results were as follows:

7.68075	gram.	CuO lost	1.55	gram.	O.	79.820	per cent.	Cu in CuO.
9.6115		"	1.939		"	79.826	"	"
						Mean, 79.823, $\pm .002$		

Erdmann and Marchand,† who come next in chronological order, corrected their results for weighing in air. Their weighings, thus corrected, give us the subjoined percentages of metal in CuO:

63.8962	gram.	CuO gave	51.0391	gram.	Cu.	79.878	per cent.
65.1590		"	52.0363		"	79.860	"
60.2878		"	48.1540		"	79.874	"
46.2700		"	36.9449		"	79.846	"
						Mean, 79.8645, $\pm .0038$	

Still later we find a few analyses by Millon and Commaille.‡ These chemists not only reduced the oxide by hydrogen, but they also weighed, in addition to the metallic copper, the water formed in the experiments. In three determinations the results were as follows:

6.7145	gram.	CuO gave	5.3565	gram.	Cu and	1.5325	gram.	H <sub>2</sub> O.	79.775	per cent.
3.3945		"	2.7085		"	.7680		"	79.791	"
2.7880		"	2.2240		"				79.770	"
										Mean, 79.7787, $\pm .0043$

For the third of these analyses the water estimation was not made, but for the other two it yielded results which, in the mean, would make the atomic weight of copper 62.680. This figure has so high a probable error that we need not consider it further.

The results obtained by Dumas§ are wholly unavailable. Indeed, he does not even publish them in detail. He merely says that he reduced copper oxide, and also effected the synthesis of the subsulphide, but without getting figures which were wholly concordant. He puts Cu = 63.5.

\* Poggend. Annal., 8, 177. 1826.

† Journ. für Prakt. Chem., 31, 380. 1844.

‡ Fresenius' Zeitschrift, 2, 475. 1863.

§ Ann. Chim. et Phys. (3), 55, 129. 1859.

In 1873 Hampe\* published his careful determinations, which were for many years almost unqualifiedly accepted. First, he attempted to estimate the atomic weight of copper by the quantity of silver which the pure metal could precipitate from its solutions. This attempt failed to give satisfactory results, and he fell back upon the old method of reducing the oxide. From ten to twenty grammes of material were taken in each experiment, and the weights were reduced to a vacuum standard :

20.3260	gram. CuO gave	16.2279	gram. Cu.	79.838	per cent.
20.68851	“	16.51669	“	79.835	“
10.10793	“	8.06926	“	79.831	“
				<hr/>	
				Mean, 79.8347, $\pm$ .0013	

Hampe also determined the quantity of copper in the anhydrous sulphate,  $\text{CuSO}_4$ . From 40 to 45 grammes of the salt were taken at a time, the metal was thrown down by electrolysis, and the weights were all corrected. I subjoin the results :

40.40300	gram. $\text{CuSO}_4$ gave	16.04958	gram. Cu.	39.724	per cent.
44.64280	“	17.73466	“	39.726	“
				<hr/>	
				Mean, 39.725, $\pm$ .0007	

The last series of data gives  $\text{Cu} = 62.839, \pm .0035$ , and is interesting for comparison with results obtained by Richards later.

In all of the foregoing experiments with copper oxide, that compound was obtained by ignition of the basic nitrate. But, as was shown in the chapter upon oxygen, copper oxide so prepared always carries occluded gases, which are not wholly expelled by heat. This point was thoroughly worked up by Richards† in his fourth memoir upon the atomic weight of copper, and it vitiates all the determinations previously made by this method.

By a series of experiments with copper oxide ignited at varying temperatures, and with different degrees of heat during the process of reduction, Richards obtained values for Cu ranging from 63.20 to 63.62, when  $\text{O} = 16$ . In two cases selected from this series he measured the amount of gaseous impurity, and corrected the results previously obtained. The results were as follows, with vacuum standards :

1.06253	gram. CuO gave.	.84831	gram. Cu.	79.802	per cent.
1.91656	“	1.5298	“	79.820	“
				<hr/>	
				Mean, 79.811, $\pm$ .0061	

Correcting for the occluded gases in the oxide, the sum of the two experiments gives 79.901 per cent. of copper, whence  $\text{Cu} = 63.605$ . Three

\* Fresenius' Zeitschrift, 13, 352.

† Proc. Amer. Acad., 26, 276. 1891.



other indirect results, similarly corrected, gave 79.900 per cent. Cu in CuO, or  $\text{Cu} = 63.603$ . If we assign all five experiments equal weight, and judge their value by the two detailed above, the mean percentage becomes  $79.900, \pm .0038$ . This figure need not be combined with the data given by previous observers, so far as practical purposes are concerned; but as this work is, in part at least, a study of the compensation of errors, it may not be wasted time to effect the combination, as follows:

Berzelius.....	79.823, $\pm .0020$
Erdmann and Marchand.....	79.8645, $\pm .0038$
Millon and Commaille.....	79.7787, $\pm .0043$
Hampe..	79.8347, $\pm .0013$
Richards.....	79.900, $\pm .0038$
General mean.....	79.8355, $\pm .0010$

This result is practically identical with that of Hampe, whose work receives excessive weight, as does also that of Berzelius. The oxide of copper is evidently of doubtful value in the measurement of this atomic weight.

The composition of the sulphate has been studied, not only by Hampe, but also by Baubigny\* and by Richards.† Baubigny merely ignited the anhydrous salt, weighing both it and the residual oxide, as follows:

4.022 gm. $\text{CuSO}_4$ gave 2.0035 CuO.	49.813 per cent.
2.596           "           1.293   "	49.807   "
	Mean, 49.810, $\pm .002$

The same ratio, in reverse—that is, the synthesis of the sulphate from the oxide—was investigated by Richards (p. 275), who shows that the results obtained are vitiated by the same errors which affect the copper oxide experiments previously cited. The weights given are reduced to vacuum standards. The percentage of oxide in the sulphate is stated in the third column of figures.

1.0084 gm. CuO gave 2.0235 gm. $\text{CuSO}_4$ .	49.835 per cent.
2.7292           "           5.4770   "	49.830   "
1.0144           "           2.0350   "	49.848   "
	Mean, 49.838, $\pm .0036$

The two series combine thus:

Baubigny.....	49.810, $\pm .0020$
Richards..	49.838, $\pm .0036$
General mean.....	49.816, $\pm .0017$

Here, plainly, the rigorous discussion gives Baubigny's work weight in excess of its merits.

\* Compt. Rend., 97, 906. 1883.

† Proc. Amer. Acad., 26, 240. 1891.

In the memoir by Richards now under consideration, his fourth upon copper, the greater part of his attention is devoted to the sulphate, Hampe being followed closely in order to ascertain what sources of error affected the work of the latter. Crystallized sulphate,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  was purified with every precaution and made the basis of operations. Three series of experiments were carried out, the water being determined by loss of weight upon heating, and the copper being estimated electrolytically. In the first series the following data were found, the weights being reduced to a vacuum, as in all of Richards' determinations:

	<i>CuSO<sub>4</sub>, 5 aq.</i>	<i>CuSO<sub>4</sub> at 250°.</i>	<i>Cu.</i>
1.....	2.8815	.....	.7337
2.....	2.7152	.....	.6911
3.....	3.4639	2.2184	.8817

Hence the subjoined percentages.

	<i>Water at 250°.</i>	<i>Cu in Cryst. Salt.</i>	<i>Cu in CuSO<sub>4</sub>.</i>
1.....	.....	25.462	.....
2.....	.....	25.452	.....
3.....	35.958	25.454	39.745
		<u>Mean, 25.456</u>	

In the second series of analyses, which are stated with much detail, several refinements were introduced, in order to estimate also the sulphuric acid. These will be considered later. The results, given below, are numbered consecutively with the former series.

	<i>CuSO<sub>4</sub>, 5 aq.</i>	<i>CuSO<sub>4</sub> at 260°.</i>	<i>CuSO<sub>4</sub> at 360°.</i>	<i>Cu.</i>
4 .. .. .	3.06006	1.9597	1.95637	.77886
5.....	2.81840	1.8048	.....	.71740
6.....	7.50490	4.8064	4.79826	1.90973

Hence percentages as follows:

	<i>Water, 260°.</i>	<i>Water, 360°.</i>	<i>Cu in Cryst. Salt.</i>	<i>Cu in CuSO<sub>4</sub>, 260°.</i>	<i>Ditto, 360°.</i>
4.....	35.959	36.068	25.452	39.744	39.811
5.....	35.964	.....	25.454	39.750	.....
6.....	35.957	36.065	25.446	39.733	39.799
	<u>Mean, 35.960</u>	<u>36.067</u>	<u>25.450</u>	<u>39.742</u>	<u>39.805</u>

Hampe worked with a sulphate dried at 250°, but these data show that a little water is retained at that temperature, and consequently that his results must have been too low. The third of Richards' series resembles the second, but extra precautions were taken to avoid conceivable errors.

	<i>CuSO<sub>4</sub>, 5 aq.</i>	<i>CuSO<sub>4</sub> at 260°.</i>	<i>CuSO<sub>4</sub> at 370°.</i>	<i>Cu.</i>
7.....	2.88307	.....	.....	.73380
8.....	3.62913	2.32373	.....	.92344
9.....	5.81352	.....	3.71680	1.47926

And the percentages are:

	<i>Water at 260°.</i>	<i>At 370°.</i>	<i>Cu in Cryst. Salt.</i>	<i>Cu in CuSO<sub>4</sub>.</i>
7.....	.....	.....	25.452	.....
8.....	35.970	.....	25.446	39.740 (260°)
9.....	.....	36.067	25.445	39.799 (370°)
			<hr/> 25.448	

In this series the determinations of sulphuric acid gave essentially the same results for all three samples of sulphate, although one was not dehydrated, and the others were heated to 260° and 370° respectively. Hence the loss of weight in dehydration at either temperature represents water only, and does not involve partial decomposition of the sulphate. Between 360° and 400° copper sulphate is at essentially constant weight, but further experiments indicated that even at 400° it retained traces of water, and possibly as much as .042 per cent. The last trace is not expelled until the salt itself begins to decompose.

Richards also effected two syntheses of the sulphate directly from the metal by dissolving the latter in nitric acid, then evaporating to dryness with sulphuric acid, and heating to constant weight at 400°.

.67720 gm.	Cu gave	1.7021 gm.	CuSO <sub>4</sub> .	39.786 per cent.	Cu.
1.00613	"	2.5292	"	39.781	"

If we include these percentages in a series with the data from analyses 4, 6, and 9, which gave percentages of 39.811, 39.799, and 39.799 respectively of copper in sulphate dried at 360° and upwards, the mean becomes

$$\text{CuSO}_4 : \text{Cu} :: 100 : 39.795, \pm .0036$$

Since even this result is presumably too low, the other figures from sulphate dried at 250° must be rejected. Since Hampe's work on the sulphate is affected by the same sources of error, and apparently to a still greater extent, it need not be considered farther. As for Richards' nine determinations of Cu in CuSO<sub>4</sub>.5H<sub>2</sub>O, we may take them as one series giving a mean percentage of 25.451,  $\pm .0011$ . This salt seems to retain occluded water, for the percentage of copper in it leads to a value for the atomic weight which is inconsistent with the best evidence, as will be seen later.

In the second and third series of Richards' experiments upon copper sulphate, the sulphuric acid was estimated by a method which gave valuable results. After the copper had been electrolytically precipitated, the acid which was set free was nearly neutralized by a weighed amount of pure sodium carbonate, and the slight excess remaining was determined by titration. Thus the weight of sodium carbonate equivalent to the copper was ascertained. The resulting solution of sodium sulphate was then evaporated to dryness, and a new ratio, connecting that salt with copper, was also determined. The cross ratio Na<sub>2</sub>CO<sub>3</sub> : Na<sub>2</sub>SO<sub>4</sub> has

already been utilized in a previous chapter. The results, ignoring the weights of hydrated copper sulphate, are as follows, with the experiments numbered as before :

	<i>Cu.</i>	<i>Na<sub>2</sub>CO<sub>3</sub>.</i>	<i>Na<sub>2</sub>SO<sub>4</sub></i>
4.....	.77886	1.2993	1.7411
6.....	1.90973	3.1862	4.2679
7.....	.73380	1.22427	1.63994
8.....	.92344	1.54075	.....
9.....	1.47926	.....	3.30658

Hence,

<i>Cu : Na<sub>2</sub>CO<sub>3</sub> :: 100 : x.</i>	<i>Cu : Na<sub>2</sub>SO<sub>4</sub> :: 100 : x.</i>
166.824	223.549
166.840	223.482
166.840	223.538
166.849	223.529
<hr/>	<hr/>
Mean, 166.838, $\pm$ .0035	Mean, 223.525, $\pm$ .0098

In one more experiment the sulphuric acid was weighed as barium sulphate, the latter being corrected for occluded salts. 3.1902 gm.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  gave 2.9761  $\text{BaSO}_4$ ; hence  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} : \text{BaSO}_4 :: 100 : 93.289$ . The sulphate contained 25.448 per cent. of Cu; hence  $\text{BaSO}_4 : \text{Cu} :: 93.289 : 25.448$ . Still other ratios can be deduced from Richards' work on the sulphate, but in view of the uncertainties relative to the water in the salt they are hardly worth computing.

In his third paper upon the atomic weight of copper,\* Richards studied the dibromide,  $\text{CuBr}_2$ . In preparing this salt he used hydrobromic acid made from pure materials, and further purified by ten distillations. This was saturated with copper oxide prepared from pure electrolytic copper, and the solution obtained was proved to be free from basic salts. As the crystallized compound was not easily obtained in a satisfactory condition, weighed quantities of the solution were taken for analysis, in which, after expulsion of bromine by nitric and sulphuric acids, the copper was determined by electrolysis. In other portions of solution the bromine was precipitated by silver nitrate, and weighed as silver bromide. The first preliminary series of experiments gave the subjoined results, with vacuum weights as usual :

*In 25 Grammes of Solution.*

<i>Cu.</i>	<i>AgBr.</i>
.4164	2.4599
.4164	2.4605
.4164	2.4605
.4165	2.4599

Hence 2 AgBr : Cu :: 100 : 16.927,  $\pm$  .0013.

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\* Proc. Amer. Acad., 25, 195. 1890.

The second, also preliminary series, was made with more dilute solutions, and came out as follows:

*In 25 Grammes of Solution.*

<i>Cu.</i>	<i>AgBr.</i>
.26190	1.5478
.26185	1.5477
	1.5479

Hence  $2 \text{ AgBr} : \text{Cu} :: 100 : 16.919, \pm .0012$ .

In the third series, two distinct lots of crystallized bromide were dissolved, and the solutions examined in the same way.

<i>Cu.</i>	<i>AgBr.</i>	<i>Ratio.</i>
.2500	1.4771	16.925
.5473	3.2348	16.919
		Mean, 16.922, $\pm .0020$

In the final set of analyses, the materials used were purified even more scrupulously than before, and the process was distinctly modified, as regards the determination of the bromine. The solution of the bromide was added to a solution of pure silver in nitric acid, not quite sufficient for complete precipitation. The slight excess of bromine was then determined by titration with a solution containing one gramme of silver to the litre. Thus silver proportional to the copper in the bromide was determined, and the silver bromide was weighed in a Gooch crucible as before. The results are subjoined:

*In 50 Grammes of Solution.*

<i>Cu.</i>	<i>Ag.</i>	<i>AgBr.</i>
.54755	1.8586	3.2350
.54750	1.8579	3.2340
	1.8583	3.2348

Hence  $\text{Cu} : \text{Ag}_2 :: 100 : 339.392, \pm .0108$ , and  $2 \text{ AgBr} : \text{Cu} :: 100 : 16.927, \pm .0012$ .

The latter ratio, combined with the results of the three preceding series, gives a general mean of:

$$2 \text{ AgBr} : \text{Cu} :: 100 : 16.924, \pm .0007$$

In his two earlier papers\* Richards determined the copper-silver ratio directly—that is, without the weighing of any compound of either metal. By placing pure copper in an *ice-cold* solution of silver nitrate, metallic silver is thrown down, and the weights of the two metals were in equiv-

\* Proc. Amer. Acad., 22, 346, and 23, 177. 1886 and 1887.

alent proportions. In the first paper the following results were obtained. The third column gives the value of  $x$  in the ratio  $\text{Cu} : \text{Ag}_2 : 100 : x$ .

<i>Cu Taken.</i>	<i>Ag Found.</i>	<i>Ratio.</i>
.53875	1.8192	339.527
.56190	1.9076	339.491
1.00220	3.4016	339.414
1.30135	4.4173	339.440
.99870	3.39235	339.477
1.02050	3.4646	339.500
		Mean, 339.475, $\pm .0114$

In the second paper Richards states that the silver of the fifth experiment, which had been dried at  $150^\circ$ , as were also the others, still retained water, to the extent of four-tenths milligramme in two grammes. If we assume this correction to be fairly uniform, as the concordance of the series indicates, and apply it throughout, the mean value for the ratio then becomes 339.408,  $\pm .0114$ . This procedure, however, leaves the ratio in some uncertainty, and accordingly some new determinations were made, in which the silver, collected in a Gooch crucible, was heated to incipient redness before final weighing. Copper from two distinct sources was taken, and three experiments were carried out upon one sample to two with the other. Treating both sets as one series, the results were as follows:

<i>Cu Taken.</i>	<i>Ag found.</i>	<i>Ratio.</i>
.75760	2.5713	339.40
.95040	3.2256	339.39
.75993	2.5794	339.42
1.02060	3.4640	339.42
.90460	3.0701	339.39
		Mean, 339.404, $\pm .0046$

a value practically identical with the corrected mean of the previous determinations, and with that found in the later experiments upon copper bromide.

In various electrical investigations the same ratio, the electrochemical equivalent of copper, has been repeatedly measured, and the later results of Lord Rayleigh and Mrs. Sidgewick,\* Gray,† Shaw,‡ and Vanni§ may properly be included in this discussion. As the data are somewhat differently stated, I have reduced them all to the common standard adopted above. Gray gives two sets of measurements, one made with large and the other with small metallic plates:

\* Phil. Trans., 175, 458.

† Phil. Mag. (5), 22, 389.

‡ British Assoc. Report, 1886. Abstract in Phil. Mag. (5), 23, 138.

§ Ann. der Phys. (Wiedemann's) (2), 44, 214.

<i>Rayleigh and S.</i>	<i>Gray 1.</i>	<i>Gray 2.</i>	<i>Shaw.</i>	<i>Vanni.</i>
340.483	341.297	340.252	339.68	340.483
340.832	341.413	339.674	340.05	340.600
340.367	340.815	340.020	339.84	340.367
—	340.252	339.905	339.71	340.252
340.561,	339.905	339.674	340.01	340.600
± .0935	341.064	339.328	339.94	340.136
	340.832	340.136	340.35	—
	341.297	340.136	339.82	340.406,
	341.064	340.136	340.09	± .0520
	341.413	340.020	339.84	
	—	340.020	339.90	
	340.935,	340.136	339.98	
	± .1072	—	340.14	
		339.953,	340.56	
		± .0521	339.82	
		—	—	
			339.983,	
			± .0411	

The lack of sharp concordance in these data and the consequently high probable errors seem to indicate a distinct superiority of the purely chemical method of determination over that adopted by the physicist. The eight distinct series now combine as follows :

Richards, first series corrected.....	339.408, ± .0114
Richards, second series.....	339.404, ± .0046
Richards, CuBr <sub>2</sub> series.....	339.392, ± .0108
Rayleigh and Sidgewick.....	340.561, ± .0935
Gray, with large plates.....	340.935, ± .1072
Gray, with small plates.....	339.953, ± .0521
Shaw.....	339.983, ± .0411
Vanni.....	340.406, ± .0520
General mean.....	339.411, ± .0039

If we combine Richards' three series into a general mean separately, we get 339.402, ± .0040. Hence the other determinations, having high probable errors, practically vanish from the result, and it is a matter of indifference whether they are retained or rejected.

We now have the following ratios from which to compute the atomic weight of copper :

- (1.) Percentage of Cu in CuO..... 79.8355, ± .0010
- (2.)    "    of Cu in CuSO<sub>4</sub>..... 39.795, ± .0036
- (3.)    "    of Cu in CuSO<sub>4</sub>, 5H<sub>2</sub>O.. 25.451, ± .0011
- (4.)    "    of CuO in CuSO<sub>4</sub>.... 49.816, ± .0017
- (5.) Cu : Na<sub>2</sub>CO<sub>3</sub> : : 100 : 166.838, ± .0035
- (6.) Cu : Na<sub>2</sub>SO<sub>4</sub> : : 100 : 223.525, ± .0098
- (7.) BaSO<sub>4</sub> : Cu : : 93.289 : 25.448.
- (8.) 2AgBr : Cu : : 100 : 16.924, ± .0007
- (9.) Cu : Ag<sub>2</sub> : : 100 : 339.411, ± .0039

Reducing these ratios with the subjoined data :

O = 15.879, $\pm .0003$	Na = 22.881, $\pm .0046$
Ag = 107.108, $\pm .0031$	Ba = 136.392, $\pm .0086$
S = 31.828, $\pm .0015$	AgBr = 186.452, $\pm .0054$
C = 11.920, $\pm .0004$	

We have nine values for the atomic weight of copper. Since ratio (7) depends upon one experiment only, it is necessary to assign the value derived from it arbitrary weight. This will be taken as indicated by a probable error double that of the next highest, obtained from ratio (2). The values then are as follows :

From (1).....	Cu = 62.869, $\pm .0034$
From (2).....	" = 63.022, $\pm .0070$
From (3).....	" = 63.070, $\pm .0030$
From (4).....	" = 63.003, $\pm .0042$
From (5).....	" = 63.127, $\pm .0051$
From (6).....	" = 63.128, $\pm .0050$
From (7).....	" = 63.215, $\pm .0140$
From (8).....	" = 63.110, $\pm .0032$
From (9).....	" = 63.114, $\pm .0020$
General mean.....	Cu = 63.070, $\pm .0012$

If O = 16, Cu = 63.550. If we include Hampe's analyses of copper sulphate, which gave Cu = 62.839,  $\pm .0035$ , the general mean becomes Cu = 63.046,  $\pm .0011$ .

The foregoing means, however, are significant only as showing the effect and weight of the older data upon the newer determinations of Richards. The seventh of the individual values is also interesting, for the reason that the experiment upon which it depends was published by Richards previous to his investigation of the atomic weight of barium. With the old value for Ba, 137, it gives a value for copper in close agreement with Richards' other determinations. With the new value for barium it becomes discordant, although its weight is so low that it produces no appreciable effect upon the final mean.

Rejecting values 1 to 4, inclusive, the remaining five values give a general mean of

$$\text{Cu} = 63.119, \pm .0015.$$

If O = 16, this becomes 63.600, and in the light of all the evidence these figures are to be preferred. If, again, we combine with this mean the results of Richards' work on the oxide and sulphate of copper, the final value becomes

$$\text{Cu} = 63.108, \pm .0013,$$

and with O = 16, 63.589. This departs but little from the previous mean value, but it includes data which render it, in all probability, a trifle too low. The value Cu = 63.119 will be regarded as the best.



## GOLD.

Among the early estimates of the atomic weight of gold the only ones worthy of consideration are those of Berzelius and Levol.

The earliest method adopted by Berzelius\* was that of precipitating a solution of gold chloride by means of a weighed quantity of metallic mercury. The weight of gold thus thrown down gave the ratio between the atomic weights of the two metals. In the single experiment which Berzelius publishes, 142.9 parts of Hg precipitated 93.55 of Au. Hence if  $Hg = 200$ ,  $Au = 196.397$ .

In a later investigation † Berzelius resorted to the analysis of potassioauric chloride,  $2KCl.AuCl_3$ . Weighed quantities of this salt were ignited in hydrogen; the resulting gold and potassium chloride were separated by means of water, and both were collected and estimated. The loss of weight upon ignition was, of course, chlorine. As the salt could not be perfectly dried without loss of chlorine, the atomic weight under investigation must be determined by the ratio between the  $KCl$  and the  $Au$ . If we reduce to a common standard, and compare with 100 parts of  $KCl$ , the equivalent amounts of gold will be those which I give in the last of the subjoined columns:

4.1445	gram, $K_2AuCl_5$ gave .8185	gram, $KCl$ and 2.159	gram, $Au$ .	263.775
2.2495	“ .44425	“ 1.172	“	263.815
5.1300	“ 1.01375	“ 2.67225	“	263.600
3.4130	“ .674	“ 1.77725	“	263.687
4.19975	“ .8295	“ 2.188	“	263.773

Mean, 263.730,  $\pm .026$

Still a third series of experiments by Berzelius ‡ may be included here. In order to establish the atomic weight of phosphorus he employed that substance to precipitate gold from a solution of gold chloride in excess. Between the weight of phosphorus taken and the weight of gold obtained it was easy to fix a ratio. Since the atomic weight of phosphorus has been better established by other methods, we may properly reverse this ratio and apply it to our discussion of gold. 100 parts of  $P$  precipitate the quantities of  $Au$  given in the third column:

.829	gram, $P$ precipitated 8.714	gram, $Au$ .	1051.15
.754	“ 7.930	“	1051.73

Mean, 1051.44,  $\pm .196$

Hence if  $P = 31$ ,  $Au = 195.568$ .

\* Poggend. Annalen, 8, 177.

† Lehrbuch, 5 Aufl., 3, 1212.

‡ Lehrbuch, 5 Aufl., 3, 1188.

Levol's\* estimation of the atomic weight under consideration can hardly have much value. A weighed quantity of gold was converted in a flask into  $\text{AuCl}_3$ . This was reduced by a stream of sulphur dioxide, and the resulting sulphuric acid was determined as  $\text{BaSO}_4$ . One gramme of gold gave 1.782 grm.  $\text{BaSO}_4$ . Hence  $\text{Au} = 195.06$ .

All these values may be neglected as worthless, except that derived from Berzelius'  $\text{K}_2\text{AuCl}_5$  series.

In 1886 Krüss† published the first of the recent determinations of the atomic weight under consideration, several distinct methods being recorded. First, in a solution of pure auric chloride the gold was precipitated by means of aqueous sulphurous acid. In the filtrate from the gold the chlorine was thrown down as silver chloride, and thus the ratio  $\text{Au} : 3 \text{AgCl}$  was measured. I subjoin Krüss' weights, together with a third column giving the gold equivalent to 100 parts of silver chloride:

<i>Au.</i>	<i>AgCl.</i>	<i>Ratio.</i>
7.72076	16.84737	45.828
5.68290	12.40425	45.814
3.24773	7.08667	45.828
4.49167	9.80475	45.811
3.47949	7.59300	45.825
3.26836	7.13132	45.832
5.16181	11.26524	45.821
4.86014	10.60431	45.834

Mean, 45.824,  $\pm .0020$

The remainder of Krüss' determinations were made with potassium auribromide,  $\text{KAuBr}_4$ , and with this salt several ratios were measured. The salt was prepared from pure materials, repeatedly recrystallized under precautions to exclude access of atmospheric dust, and dried over phosphorus pentoxide. First, its percentage of gold was determined, sometimes by reduction with sulphurous acid, sometimes by heating in a stream of hydrogen. For this ratio, the weights and percentages are as follows, the experiments being numbered for further reference, and the reducing agent being indicated.

	<i>K.AuBr<sub>4</sub>.</i>	<i>Au.</i>	<i>Per cent.</i>
1. $\text{SO}_2$ .....	10.64821	3.77753	35.476
2. $\text{SO}_2$ .....	4.71974	1.67330	35.453
3. H.....	7.05762	2.50122	35.440
4. H.....	4.49558	1.59434	35.465
5. $\text{SO}_2$ .....	8.72302	3.09448	35.475
6. $\text{SO}_2$ .....	7.66932	2.71860	35.448
7. $\text{SO}_2$ .....	7.15498	2.53695	35.457
8. H.....	12.26334	4.34997	35.471
9. H.....	7.10342	2.51919	35.465

Mean, 35.461,  $\pm .0025$

\* Ann. Chim. Phys. (3), 30, 355. 1850.

† Untersuchungen über das Atomgewicht des Goldes. München, 1886. 112 pp., 8vo.

In five of the foregoing experiments the reductions were effected with sulphurous acid; and in these, after filtering off the gold, the bromine was thrown down and weighed as silver bromide. This, in comparison with the gold, gives the ratio  $\text{Au} : 4\text{AgBr} :: 100 : x$ .

	<i>Au.</i>	<i>4AgBr.</i>	<i>Ratio.</i>
1.....	3.77753	14.39542	381.080
2 .....	1.67330	6.37952	381.254
5.....	3.09448	11.78993	380.999
6 .....	2.71860	10.35902	381.042
7.....	2.53695	9.66117	380.731

Mean, 381.021,  $\pm .057$

Hence  $\text{Au} : \text{AgBr} :: 100 : 95.255, \pm .0142$ .

In the remaining experiments, Nos. 3, 4, 8, and 9, the  $\text{KAuBr}_4$  was reduced in a stream of hydrogen, the loss of weight,  $\text{Br}_3$ , being noted. In the residue the gold was determined, as noted above, and the  $\text{KBr}$  was also collected and weighed. The weights were as follows:

	<i>Au.</i>	<i>Loss, Br<sub>3</sub>.</i>	<i>KBr.</i>
3.....	2.50122	3.04422	1.51090
4.....	1.59434	1.93937	.96243
8 .....	4.34997	5.29316	2.62700
9....	2.51919	3.06534	1.52153

From these data we obtain two more ratios, viz.,  $\text{Au} : \text{Br}_3 :: 100 : x$ , and  $\text{Au} : \text{KBr} :: 100 : x$ , thus:

	<i>Au : Br<sub>3</sub>.</i>	<i>Au : KBr.</i>
3 .....	121.710	60.405
4....	121.641	60.365
8 . ....	121.683	60.391
9.....	121.680	60.398

Mean, 121.678,  $\pm .0100$

Mean, 60.390,  $\pm .0059$

From all the ratios, taken together, Krüss deduces a final value of  $\text{Au} = 197.13$ , if  $\text{O} = 16$ . It is obviously possible to derive still other ratios from the results given, but to do so would be to depart unnecessarily from the author's methods as stated by himself.

Thorpe and Laurie,\* whose work appeared shortly after that of Krüss, also made use of the salt  $\text{KAuBr}_4$ , but, on account of difficulty in drying it without change, they did not weigh it directly. After proving the constancy in it of the ratio  $\text{Au} : \text{KBr}$ , even after repeated crystallizations, they adopted the following method: The unweighed salt was heated with gradual increase of temperature, up to about  $160^\circ$ , for several hours, and afterwards more strongly over a small Bunsen flame. This was done in a porcelain crucible, tared by another in weighing, which latter was treated in precisely the same way. The residue,  $\text{KBr} + \text{Au}$ , was weighed, the  $\text{KBr}$  dissolved out, and the gold then weighed separately. The

\* Journ. Chem. Soc., 51, 565. 1887.

weight of KBr was taken by difference. The ratio  $\text{Au} : \text{KBr} :: 100 : x$  appears in a third column.

<i>Au.</i>	<i>KBr.</i>	<i>Ratio.</i>
6.19001	3.73440	60.329
4.76957	2.87715	60.323
4.14050	2.49822	60.336
3.60344	2.17440	60.342
3.67963	2.21978	60.326
4.57757	2.76195	60.337
5.36659	3.23821	60.326
5.16406	3.11533	60.327

Mean, 60.331,  $\pm .0016$

This mean combines with Krüss' thus:

Krüss.....	60.390, $\pm .0059$
Thorpe and Laurie.....	60.331, $\pm .0016$
General mean.....	60.338, $\pm .0015$

The potassium bromide of the previous experiments was next titrated with a solution of pure silver by Stas' method, the operation being performed in red light. Thus we get the following data for the ratio  $\text{Ag} : \text{Au} :: 100 : x$ , using the weights of gold already obtained:

<i>Ag.</i>	<i>Au.</i>	<i>Ratio.</i>
3.38451	6.19001	182.893
2.60896	4.76957	182.813
2.28830	4.18266	182.786
2.26415	4.14050	182.868
1.97147	3.60344	182.775
2.01292	3.67963	182.801
2.50334	4.57757	182.863
2.93608	5.36659	182.780
2.82401	5.16406	182.865

Mean, 182.827,  $\pm .0101$

Finally, in eight of these experiments, the silver bromide formed during titration was collected and weighed, giving values for the ratio  $\text{Au} : \text{AgBr} :: 100 : x$ , as follows:

<i>Au.</i>	<i>AgBr.</i>	<i>Ratio.</i>
6.19001	5.89199	95.186
4.76957	4.54261	95.242
4.18266	3.98288	95.224
4.14050	3.94309	95.232
3.60344	3.43015	95.191
3.67963	3.50207	95.175
4.57757	4.35736	95.189
5.36659	5.11045	95.227

Mean, 95.208,  $\pm .0061$

Krüss found, 95.255,  $\pm .0142$

General mean, 95.222,  $\pm .0056$

From the second and third of the ratios measured by Thorpe and Laurie an independent value for the ratio  $\text{Ag} : \text{Br}$  may be computed. It becomes  $100 : 74.072$ , which agrees closely with the determinations made by Stas and Marignac. Similarly, the ratios  $\text{Ag} : \text{KBr}$  and  $\text{AgBr} : \text{KBr}$  may be calculated, giving additional checks upon the accuracy of the manipulation, though not upon the purity of the original material studied.

Thorpe and Laurie suggest objections to the work done by Krüss, on the ground that the salt  $\text{KAuBr}_4$  cannot be completely dried without loss of bromine. This suggestion led to a controversy between them and Krüss, which in effect was briefly as follows:

First, Krüss\* urges that the potassium auribromide ordinarily contains traces of free gold, not belonging to the salt, produced by the reducing action of dust particles taken up from the air. He applies a correction for this supposed free gold to the determinations made by Thorpe and Laurie, and thus brings their results into harmony with his own. To this argument Thorpe and Laurie† reply, somewhat in detail, stating that the error indicated was guarded against by them, and that they had dissolved quantities of from eight to nineteen grammes of the auribromide without a trace of free gold becoming visible. A final note in defense of his own work was published by Krüss a little later.‡

In 1889 an elaborate set of determinations of this constant was published by Mallet,§ whose experiments are classified into seven distinct series. First, a neutral solution of auric chloride was prepared, which was weighed off in two approximately equal portions. In one of these the gold was precipitated by pure sulphurous acid, collected, washed, dried, ignited in a Sprengel vacuum, and weighed. To the second portion a solution containing a known weight of pure silver was added. After filtering, with all due precautions, the silver remaining in the filtrate was determined by titration with a weighed solution of pure hydrobromic acid. We have thus a weight of gold, and the weight of silver needed to precipitate the three atoms of chlorine combined with it: in other words, the ratio  $\text{Ag}_3 : \text{Au} :: 100 : x$ . All weights in this and the subsequent series are reduced to vacuum standards, and all weighings were made against corresponding tares.

<i>Au.</i>	<i>Ag<sub>3</sub>.</i>	<i>Ratio.</i>
7.6075	12.4875	60.921
8.4212	13.8280	60.900
6.9407	11.3973	60.898
3.3682	5.5286	60.923
2.8244	4.6371	60.909

Mean, 60.910,  $\pm .0034$

Hence  $\text{Ag} : \text{Au} :: 100 : 182.730, \pm .0102$ .

\* Ber. Deutsch. Chem. Gesell., 20, 2365. 1887.

† Berichte, 20, 3036, and Journ. Chem. Soc., 51, 866. 1887.

‡ Berichte, 21, 126. 1888.

§ Philosophical Transactions, 180, 395. 1889.

The second series of determinations was essentially like the first, except that auric bromide was taken instead of the chloride. The ratio measured,  $\text{Ag}_3 : \text{Au}$ , is precisely the same as before. Results as follows:

<i>Au.</i>	<i>Ag<sub>3</sub>.</i>	<i>Ratio.</i>
8.2345	13.5149	60.929
7.6901	12.6251	60.911
10.5233	17.2666	60.945
2.7498	4.5141	60.916
3.5620	5.8471	60.919
3.9081	6.4129	60.941

Mean, 60.927,  $\pm .0038$

Hence  $\text{Ag} : \text{Au} :: 100 : 182.781, \pm .0114$ .

In the third series of experiments the salt  $\text{KAuBr}_4$  was taken, purified by five recrystallizations. The solution of this was weighed out into nearly equal parts, the gold being measured as in the two preceding series in one portion, and the bromine thrown down by a standard silver solution as before. This gives the ratio  $\text{Ag}_4 : \text{Au} :: 100 : x$ .

<i>Au.</i>	<i>Ag.</i>	<i>Ratio.</i>
5.7048	12.4851	45.693
7.9612	17.4193	45.693
2.4455	5.3513	45.690
4.1632	9.1153	45.673

Mean, 45.689,  $\pm .0040$

Hence  $\text{Ag} : \text{Au} :: 100 : 182.756, \pm .0160$ .

The fifth series of determinations, which for present purposes naturally precedes the fourth, was electrolytic in character, gold and silver being simultaneously precipitated by the same current. The gold was in solution as potassium auro-cyanide, and the silver in the form of potassium silver cyanide. The equivalent weights of the two metals, thrown down in the same time, were as follows, giving directly the ratio  $\text{Ag} : \text{Au} :: 100 : x$ .

<i>Au.</i>	<i>Ag.</i>	<i>Ratio.</i>
5.2721	2.8849	182.748
6.3088	3.4487	182.933
4.2770	2.3393	182.832
3.5123	1.9223	182.713
3.6804	2.0132	182.814

Mean, 182.808,  $\pm .0256$

This mean may be combined with the preceding means, and also with the determination of the same ratio by Thorpe and Laurie, thus:

Thorpe and Laurie.....	182.827, $\pm .0101$
Mallet, chloride series. ....	182.730, $\pm .0102$
Mallet, bromide series. ....	182.781, $\pm .0114$
Mallet, $\text{KAuBr}_4$ series.....	182.756, $\pm .0160$
Mallet, electrolytic.....	182.808, $\pm .0256$
General mean.....	182.778, $\pm .0055$

In Mallet's fourth series a radically new method was employed. Trimethyl-ammonium aurichloride,  $N(CH_3)_3HAuCl_4$ , was decomposed by heat, and the residual gold was determined. In order to avoid loss by spattering, the salt was heated in a crucible under a layer of fine siliceous sand of known weight. Several crops of crystals of the salt were studied, as a check against impurities, but all gave concordant values.

<i>Salt.</i>	<i>Residual Au.</i>	<i>Per cent. Au.</i>
14.9072	7.3754	49.475
15.5263	7.6831	49.484
10.4523	5.1712	49.474
6.5912	3.2603	49.464
5.5744	2.7579	49.474

Mean, 49.474,  $\pm .0021$

In his sixth and seventh series Mallet seeks to establish, by direct measurement, the ratio between hydrogen and gold. In their experimental details his methods are somewhat elaborate, and only the processes, in the most general way, can be indicated here. First, gold was precipitated electrolytically from a solution of potassium aurocyanide, and its weight was compared with that of the amount of hydrogen simultaneously liberated in a voltameter by the same current in the same time. The hydrogen was measured, and its weight was then computed from its density. The volumes are given, of course, at  $0^\circ$  and 760 mm.

<i>Wt. Au.</i>	<i>Vol. H, cc.</i>	<i>Wt. H.</i>
4.0472	228.64	.0205483
4.0226	227.03	.0204046
4.0955	231.55	.0208103

These data, with the weight of one litre of hydrogen taken as 0.89872 gramme, give the subjoined values in the ratio  $H : Au :: 1 : x$ .

196.960
197.151
196.805

Mean, 196.972,  $\pm .0675$

In the last series of experiments a known quantity of metallic zinc was dissolved in dilute sulphuric acid, and the amount of hydrogen evolved was measured. Then a solution of pure auric chloride or bromide was treated with a definite weight of the same zinc, and the quantity of gold thrown down was determined. The zinc itself was purified by practical distillation in a Sprengel vacuum. From these data the ratio  $H_2 : Au$  was computed by direct comparison of the weight of gold and that of the liberated hydrogen. The results were as follows :

<i>Wt. Au.</i>	<i>Vol. H, cc.</i>	<i>Wt. H.</i>
10.3512	1756.10	.157824
8.2525	1400.38	.125857
8.1004	1374.87	.123565
3.2913	558.64	.050206
3.4835	590.93	.053109
3.6421	618.11	.055551

Hence for the ratio  $H_2 : Au :: 1 : x$  we have :

65.587
65.571
65.557
65.556
65.593
65.563
<hr/>
Mean, 65.571, $\pm .00436$

And  $H : Au :: 1 : 196.713, \pm .0131$ . This, combined with the value found in the preceding series, gives a general mean of  $196.722, \pm .0129$ .

The ratios available for gold are now as follows :

- (1.)  $2KCl : Au :: 100 : 263.730, \pm .026$
- (2.)  $3AgCl : Au :: 100 : 45.824, \pm .0020$
- (3.)  $KAuBr_4 : Au :: 100 : 35.461, \pm .0028$
- (4.)  $Au : AgBr :: 100 : 95.222, \pm .0056$
- (5.)  $Au : Br_3 :: 100 : 121.678, \pm .0100$
- (6.)  $Au : KBr :: 100 : 60.338, \pm .0015$
- (7.)  $Ag : Au :: 100 : 182.778, \pm .0055$
- (8.)  $NC_3H_{10}AuCl_4 : Au :: 100 : 49.474, \pm .0021$
- (9.)  $H : Au :: 1 : 196.722, \pm .0129$

For the reduction of these ratios the antecedent data are :

Ag = 107.108, $\pm .0031$	C = 11.920, $\pm .0004$
Cl = 35.179, $\pm .0048$	AgCl = 142.287, $\pm .0037$
Br = 79.344, $\pm .0062$	AgBr = 186.452, $\pm .0054$
K = 38.817, $\pm .0051$	KCl = 74.025, $\pm .0019$
N = 13.935, $\pm .0021$	KBr = 118.200, $\pm .0073$

Hence for the atomic weight of gold we have nine values :

From (1) .....	Au = 195.226, $\pm .0193$
From (2) .....	" = 195.605, $\pm .0099$
From (3) .....	" = 195.711, $\pm .0224$
From (4) .....	" = 195.808, $\pm .0126$
From (5) .....	" = 195.624, $\pm .0222$
From (6) .....	" = 195.896, $\pm .0131$
From (7) .....	" = 195.770, $\pm .0082$
From (8) .....	" = 196.238, $\pm .0224$
From (9) .....	" = 196.722, $\pm .0129$

General mean ..... Au = 195.850,  $\pm .0044$

If  $O = 16$ , this becomes  $Au = 197.342$ .



Of the foregoing values the first one, which is derived from Berzelius' work, should certainly be rejected. So also, apparently, should the eighth and ninth values. Excluding these, values 2 to 7, inclusive, give a general mean of  $\text{Au} = 195.743, \pm .0049$ . With  $\text{O} = 16$ , this becomes  $\text{Au} = 197.235$ . Probably these values are more nearly correct than those which include all the determinations.

The ninth value in the list given above represents Mallet's comparisons of gold directly with hydrogen, and is peculiarly instructive. In Mallet's paper the other determinations are discussed upon the basis of  $\text{O} = 15.96$ , which brings them more nearly into harmony with the hydrogen series. The great divergence shown in this recalculation is due to the new value for oxygen, 15.879, and its effect upon the atomic weights of silver, bromine, etc. The former agreement between the several series of gold values was therefore only apparent, and we are now able to see that concordance among determinations may be only coincidence, and no proof of accuracy. It is probable, furthermore, that direct comparisons of metals with hydrogen cannot give good measurements of atomic weights, for several reasons. First, it is not possible to be certain that every trace of hydrogen has been collected and measured, and any loss tends to raise the apparent atomic weight of the metal studied; secondly, the weight of the hydrogen is computed from its volume, and a slight change in the factors used in reduction of the observations may make a considerable difference in the final result. These uncertainties exist in all determinations of atomic weights hitherto made by the hydrogen method.

## CALCIUM.

For determining the atomic weight of calcium we have sets of experiments by Berzelius, Erdmann and Marchand, and Dumas. Salvétat\* also has published an estimation, but without the details necessary to enable us to make use of his results. I also find a reference† to some work of Marignac, which, however, seems to have been of but little importance. The earlier work of Berzelius was very inexact as regards calcium, and it is not until we come down to the year 1824 that we find any material of decided value.

The most important factor in our present discussion is the composition of calcium carbonate, as worked out by Dumas and by Erdmann and Marchand.

In 1842 Dumas‡ made three ignitions of Iceland spar, and determined the percentages of carbon dioxide driven off and of lime remaining. The impurities of the material were also determined, the correction for them applied, and the weighings reduced to a vacuum standard. The percentage of lime came out as follows :

$$\begin{array}{r} 56.12 \\ 56.04 \\ 56.06 \\ \hline \text{Mean, } 56.073, \pm .016 \end{array}$$

About this same time Erdmann and Marchand§ began their researches upon the same subject. Two ignitions of spar, containing .04 per cent. of impurity, gave respectively 56.09 and 56.18 per cent. of residue; but these results are not exact enough for us to consider further. Four other results obtained with artificial calcium carbonate are more noteworthy. The carbonate was precipitated from a solution of pure calcium chloride by ammonium carbonate, was washed thoroughly with hot water, and dried at a temperature of 180°. With this preparation the following residues of lime were obtained :

$$\begin{array}{r} 56.03 \\ 55.98 \\ 56.00 \\ 55.99 \\ \hline \text{Mean, } 56.00, \pm .007 \end{array}$$

It was subsequently shown by Berzelius that calcium carbonate prepared by this method retains traces of water even at 200°, and that

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\* Compt. Rend., 17, 318. 1843.

† See Oudemans's monograph, p. 51.

‡ Compt. Rend., 14, 537. 1842.

§ Journ. für Prakt. Chem., 26, 472. 1842.

minute quantities of chloride are also held by it. These sources of error are, however, in opposite directions, since one would tend to diminish and the other to increase the weight of residue.

In the same paper there are also two direct estimations of carbonic acid in pure Iceland spar, which correspond to the following percentages of lime :

$$\begin{array}{r} 56.00 \\ 56.02 \\ \hline \text{Mean, } 56.01, \pm .007 \end{array}$$

In a still later paper\* the same investigators give another series of results based upon the ignition of Iceland spar. The impurities were carefully estimated, and the percentages of lime are suitably corrected :

4.2134 gm. $\text{CaCO}_3$ gave	2.3594 gm. $\text{CaO}$ .	55.997 per cent.
15.1385        "	8.4810        "	56.022        "
23.5503        "	13.1958       "	56.031        "
23.6390        "	13.2456       "	56.032        "
42.0295        "	23.5533       "	56.044        "
49.7007        "	27.8536       "	56.042        "
		<u>Mean, 56.028, <math>\pm</math> .0047</u>

Six years later Erdmann and Marchand† published one more result upon the ignition of calcium carbonate. They found that the compound began giving off carbon dioxide below the temperature at which their previous samples had been dried, or about  $200^\circ$ , and that, on the other hand, traces of the dioxide were retained by the lime after ignition. These two errors do not compensate each other, since both tend to raise the percentage of lime. In the one experiment now under consideration these errors were accurately estimated, and the needful corrections were applied to the final result. The percentage of residual lime in this case came out 55.998. This agrees tolerably well with the figures found in the direct estimation of carbonic acid, and, if combined with those two, gives a mean for all three of 56.006,  $\pm$  .0043.

Combining all these series, we get the following result :

Dumas.....	56.073, $\pm$ .016
Erdmann and Marchand.....	56.006, $\pm$ .007
Erdmann and Marchand.....	56.028, $\pm$ .0047
Erdmann and Marchand.....	56.006, $\pm$ .0043
General mean.....	<u>56.0198, <math>\pm</math> .0029</u>

For reasons given above, this mean is probably vitiated by a slight constant error, which makes the figure a trifle too high.

\* Journ. für Prakt. Chem., 31, 269. 1844.

† Journ. für Prakt. Chem., 50, 237. 1850.

In the earliest of the three papers by Erdmann and Marchand there is also given a series of determinations of the ratio between calcium carbonate and sulphate. Pure Iceland spar was carefully converted into calcium sulphate, and the gain in weight noted. One hundred parts of spar gave of sulphate:

136.07	
136.06	
136.02	
136.06	
<hr/>	
Mean, 136.0525, $\pm .0071$	

In 1843 the atomic weight of calcium was redetermined by Berzelius,\* who investigated the ratio between lime and calcium sulphate. The calcium was first precipitated from a pure solution of nitrate by means of ammonium carbonate, and the thoroughly washed precipitate was dried and strongly ignited in order to obtain lime wholly free from extraneous matter. This lime was then, with suitable precautions, treated with sulphuric acid, and the resulting sulphate was weighed. Correction was applied for the trace of solid impurity contained in the acid, but not for the weighing in air. The figures in the last column represent the percentage of weight gained by the lime upon conversion into sulphate:

1.80425 gm. CaO gained	2.56735 gm.	142.295
2.50400       "       "	3.57050       "	142.592
3.90000       "       "	5.55140       "	142.343
3.04250       "       "	4.32650       "	142.202
3.45900       "       "	4.93140       "	142.567
		<hr/>
		Mean, 142.3998, $\pm .0518$

Last of all we have the ratio between calcium chloride and silver, as determined by Dumas.† Pure calcium chloride was first ignited in a stream of dry hydrochloric acid, and the solution of this salt was afterwards titrated with a silver solution in the usual way. The  $\text{CaCl}_2$  proportional to 100 parts of Ag is given in a third column:

2.738 gm. $\text{CaCl}_2 =$	5.309 gm. Ag.	51.573
2.436       "       "	4.731       "	51.490
1.859       "       "	3.617       "	51.396
2.771       "       "	5.3885       "	51.424
2.240       "       "	4.3585       "	51.394
		<hr/>
		Mean, 51.4554, $\pm .0230$

We have now four ratios to compute from, as follows:

- (1.) Percentage CaO in  $\text{CaCO}_3$ , 56.0198,  $\pm .0029$
- (2.)  $\text{CaO} : \text{SO}_3 :: 100 : 142.3998$ ,  $\pm .0518$
- (3.)  $\text{CaCO}_3 : \text{CaSO}_4 :: 100 : 136.0525$ ,  $\pm .0071$
- (4.)  $\text{Ag}_2 : \text{CaCl}_2 :: 100 : 51.4554$ ,  $\pm .0230$

\* Journ. für Prakt. Chem., 31, 263. Ann. Chem. Pharm., 46, 241.

† Ann. Chim. Phys. (3), 55, 129. 1859. Ann. Chem. Pharm., 113, 34.

The antecedent values are—

O = 15.879, $\pm$ .0003	C = 11.920, $\pm$ .0004
Ag = 107.108, $\pm$ .0031	S = 31.828, $\pm$ .0015
Cl = 35.179, $\pm$ .0048	

Hence the subjoined values for the atomic weight of calcium :

From (1).....	Ca = 39.757, $\pm$ .0048
From (2)... ..	“ = 39.925, $\pm$ .0203
From (3).....	“ = 39.706, $\pm$ .0204
From (4).....	“ = 39.868, $\pm$ .0503
Mean.....	Ca = 39.764, $\pm$ .0045

If O = 16, Ca = 40.067.

## STRONTIUM.

The ratios which fix the atomic weight of strontium resemble in general terms those relating to barium, only they are fewer in number and represent a smaller amount of work. The early experiments of Stromeyer,\* who measured the volume of CO<sub>2</sub> evolved from a known weight of strontium carbonate, are hardly available for the present discussion. So also we may exclude the determination by Salvétat,† who neglected to publish sufficient details.

Taking the ratio between strontium chloride and silver first in order, we have series of figures by Pelouze and by Dumas. Pelouze‡ employed the volumetric method to be described under barium, and in two experiments obtained the subjoined results. In another column I append the ratio between SrCl<sub>2</sub> and 100 parts of silver :

1.480 gm. SrCl <sub>2</sub> = 2.014 gm. Ag.	73.486
2.210        “        3.008        “	73.471
	Mean, 73.4781, $\pm$ .0050

Dumas.§ by the same general method, made sets of experiments with three samples of chloride which had previously been fused in a current of dry hydrochloric acid. His results, expressed in the usual way, are as follows :

\* Schweigg. Journ., 19, 228. 1816.

† Compt. Rend., 17, 318. 1843.

‡ Compt. Rend., 20, 1047. 1845.

§ Ann. Chim. Phys. (3), 55, 29. 1859. Ann Chem. Pharm., 113, 34.

*Series A.*

3.137	gram.	$\text{SrCl}_2 = 4.280$	gram.	Ag.	Ratio, 73.2944
1.982	"	2.705	"	"	73.2717
3.041	"	4.142	"	"	73.4186
3.099	"	4.219	"	"	73.4534
					<hr/>
					Mean, 73.3595

*Series B.*

3.356	gram.	$\text{SrCl}_2 = 4.574$	gram.	Ag.	Ratio, 73.3713
6.3645	"	8.667	"	"	73.4327
7.131	"	9.712	"	"	73.4246
					<hr/>
					Mean, 73.4095

*Series C.*

7.213	gram.	$\text{SrCl}_2 = 9.811$	gram.	Ag.	Ratio, 73.5195
2.206	"	3.006	"	"	73.3866
4.268	"	5.816	"	"	73.5529
4.018	"	5.477	"	"	73.3613
					<hr/>
					Mean, 73.4551

Mean of all as one series, 73.4079,  $\pm .0170$

Combining these data we have:

Pelouze .....	73.4781, $\pm .0050$
Marignac.....	73.4079, $\pm .0170$
<hr/>	
General mean.....	73.4725, $\pm .0048$

The foregoing figures apply to anhydrous strontium chloride. The ratio between silver and the crystallized salt,  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ , has also been determined in two series of experiments by Marignac.\* Five grammes of salt were used in each estimation, and, in the second series, the percentage of water was first determined. The quantities of the salt corresponding to 100 parts of silver are given in the last column:

*Series A.*

5	gram.	$\text{SrCl}_2 \cdot 6\text{H}_2\text{O} = 4.0515$	gram.	Ag.	123.411
"	"	4.0495	"	"	123.472
"	"	4.0505	"	"	123.442
					<hr/>
					Mean, 123.442

*Series B.*

5	gram.	$\text{SrCl}_2 \cdot 6\text{H}_2\text{O} = 4.0490$	gram.	Ag.	123.487
"	"	4.0500	"	"	123.457
"	"	4.0490	"	"	123.487
					<hr/>
					Mean, 123.477

Mean of all as one series, 123.460,  $\pm .0082$

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\* Journ. für Prakt. Chem., 74, 216. 1858.

In the same paper Marignac gives two sets of determinations of the percentage of water in crystallized strontium chloride. The first set, corresponding to "B" above, is as follows:

40.556
40.568
40.566
<hr/>
Mean, 40.563

In the second set ten grammes of salt were taken at a time, and the following percentages were found:

40.58
40.59
40.58
<hr/>
Mean, 40.583
Mean of all as one series, 40.573, $\pm .0033$

The chloride used in the series of estimations last given was subsequently employed for ascertaining the ratio between it and the sulphate. Converted directly into sulphate, 100 parts of chloride yield the quantities given in the third column:

5.942 gm. $\text{SrCl}_2$ gave 6.887 gm. $\text{SrSO}_4$ .	115.932
5.941        "        6.8855        "	115.949
5.942        "        6.884        "	115.927
<hr/>	
Mean, 115.936, $\pm .004$	

Richards,\* in his study of strontium bromide, followed pretty much the lines laid down in his work on barium. The properties of the bromide itself were carefully investigated, and its purity established beyond reasonable doubt, and then the two usual ratios were determined. First, the ratio  $\text{Ag}_2 : \text{SrBr}_2 :: 100 : x$ , by titration with standard solutions of silver. For this ratio there are three series of measurements, by varied processes, concerning which full details are given. The data obtained, with weights reduced to a vacuum, are as follows:

*First Series.*

<i>Wt. Ag.</i>	<i>Wt. <math>\text{SrBr}_2</math>.</i>	<i>Ratio.</i>
1.30755	1.49962	114.689
2.10351	2.41225	114.677
2.23357	2.56153	114.683
5.3684	6.15663	114.683
		<hr/>
		Mean, 114.683

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\* Proc. Amer. Acad. of Sciences, 1894, p. 369.

*Second Series.*

<i>Wt. Ag.</i>	<i>Wt. SrBr<sub>2</sub>.</i>	<i>Ratio.</i>
1.30762	1.49962	114.683
2.10322	2.41225	114.693
4.57502	5.24727	114.694
5.3680	6.15663	114.691
		<hr/>
		Mean, 114.690

*Third Series.*

2.5434	2.9172	114.697
3.3957	3.8946	114.692
3.9607	4.5426	114.692
4.5750	5.2473	114.695
		<hr/>
		Mean, 114.694
Mean of all as one series, 114.689, $\pm .0012$		

For the ratio, measured gravimetrically,  $2\text{AgBr} : \text{SrBr}_2 :: 100 : x$ , two series of determinations are given :

*First Series.*

<i>Wt. AgBr.</i>	<i>Wt. SrBr<sub>2</sub>.</i>	<i>Ratio.</i>
2.4415	1.6086	65.886
2.8561	1.8817	65.884
6.9337	4.5681	65.883
		<hr/>
		Mean, 65.884

*Second Series.*

2.27625	1.49962	65.881
3.66140	2.41225	65.883
3.88776	2.56153	65.887
9.34497	6.15663	65.882
		<hr/>
		Mean, 65.883
Mean of all as one series, 65.884, $\pm .0006$		

For the atomic weight of strontium we now have the subjoined ratios :

- (1.)  $\text{Ag}_2 : \text{SrCl}_2 :: 100 : 73.4725, \pm .0048$
- (2.)  $\text{Ag}_2 : \text{SrCl}_2.6\text{H}_2\text{O} :: 100 : 123.460, \pm .0082$
- (3.) Per cent.  $\text{H}_2\text{O}$  in  $\text{SrCl}_2.6\text{H}_2\text{O}$ ,  $40.573, \pm .0033$
- (4.)  $\text{SrCl}_2 : \text{SrSO}_4 :: 100 : 115.936, \pm .0040$
- (5.)  $\text{Ag}_2 : \text{SrBr}_2 :: 100 : 114.689, \pm .0012$
- (6.)  $2\text{AgBr} : \text{SrBr}_2 :: 100 : 65.884, \pm .0006$

The antecedent values are—

O = 15.879, $\pm .0003$	Br = 79.344, $\pm .0062$
Ag = 107.108, $\pm .0031$	S = 31.828, $\pm .0015$
Cl = 35.179, $\pm .0048$	AgBr = 186.452, $\pm .0054$



For the molecular weight of  $\text{SrCl}_2$  three estimates are available :

From (1).....	$\text{SrCl}_2 = 157.390, \pm .0112$
From (2).....	" = $157.197, \pm .0192$
From (3).....	" = $157.123, \pm .0157$
<hr/>	
General mean.....	$\text{SrCl}_2 = 157.281, \pm .0083$

For  $\text{SrBr}_2$  there are two values :

From (5).....	$\text{SrBr}_2 = 245.682, \pm .0076$
From (6).....	" = $245.684, \pm .0075$
<hr/>	
General mean.....	$\text{SrBr}_2 = 245.683, \pm .0053$

Finally, with these intermediate data we obtain three independent measures of the atomic weight of strontium, as follows :

From molecular weight $\text{SrCl}_2$ .....	$\text{Sr} = 86.923, \pm .0127$
From molecular weight $\text{SrBr}_2$ .....	" = $86.995, \pm .0135$
From ratio (4).....	" = $86.434, \pm .0811$
<hr/>	
General mean.....	$\text{Sr} = 86.948, \pm .0092$

If  $\text{O} = 16$ ,  $\text{Sr} = 87.610$ . Rejection of the third value, which is worthless, raises these means by 0.01 only. The second value, 86.995, which represents Richards' work, is undoubtedly the best of the three.

## BARIUM.

For the atomic weight of barium we have a series of eight ratios, established by the labors of Berzelius, Turner, Struve, Marignac, Dumas, and Richards. Andrews\* and Salyétat,† in their papers upon this subject, gave no details nor weighings, and therefore their work may be properly disregarded. First in order, we may consider the ratio between silver and barium chloride, as determined by Pelouze, Marignac, Dumas, and Richards.

Pelouze, ‡ in 1845, made the three subjoined estimations of this ratio, using his well known volumetric method. A quantity of pure silver was dissolved in nitric acid, and the amount of barium chloride needed to precipitate it was carefully ascertained. In the last column I give the quantity of barium chloride proportional to 100 parts of silver:

3.860 grm. BaCl <sub>2</sub> ppt.	4.002 grm. Ag.	96.452
5.790           "	6.003       "	96.452
2.895           "	3.001       "	96.468

Mean, 96.4573,  $\pm$  .0036

Essentially the same method was adopted by Marignac § in 1848. His experiments were made upon four samples of barium chloride, as follows. A, commercial barium chloride, purified by recrystallization from water. B, the same salt, calcined, redissolved in water, the solution saturated with carbonic acid, filtered, and allowed to crystallize. C, the preceding salt, washed with alcohol, and again recrystallized. D, the same, again washed with alcohol. For 100 parts of silver the following quantities of chloride were required, as given in the third column:

	<i>Ag.</i>	<i>BaCl<sub>2</sub>.</i>	<i>Ratio.</i>	
A.	3.4445	3.3190	96.356	} Mean, 96.354
	3.7480	3.6110	96.345	
	6.3446	6.1140	96.362	
B.	4.3660	4.1780	96.356	} Mean, 96.354
	4.8390	4.6625	96.352	
C.	6.9200	6.6680	96.358	} Mean, 96.360
	5.6230	5.4185	96.363	
D.	5.8435	5.6300	96.346	} Mean, 96.367
	8.5750	8.2650	96.384	
	4.8225	4.6470	96.361	
	6.8460	6.5980	96.377	

Mean, 96.360,  $\pm$  .0024

\* Chemical Gazette, October, 1852.

† Compt. Rend., 17, 318.

‡ Compt. Rend., 20, 1047. Journ. für Prakt. Chem., 35, 73.

§ Arch. d. Sci. Phys. et Nat., 8, 271.

Dumas\* employed barium chloride prepared from pure barium nitrate, and took the extra precaution of fusing the salt at a red heat in a current of dry hydrochloric acid gas. Three series of experiments upon three samples of chloride gave the following results :

	<i>Ag.</i>	<i>BaCl<sub>2</sub>.</i>	<i>Ratio.</i>	
A.	1.8260	1.7585	96.303	} Mean, 96.333
	3.9980	3.8420	96.339	
	2.2405	2.1585	96.340	
	4.1680	4.0162	96.358	
B.	1.7270	1.6625	96.265	} Mean, 96.290
	2.5946	2.4987	96.304	
	3.5790	3.4468	96.306	
	4.2395	4.0822	96.290	
	4.3683	4.2062	96.289	
	4.6290	4.4564	96.271	
	9.0310	8.6975	96.307	
C.	2.3835	2.2957	96.316	} Mean, 96.338
	4.2930	4.1372	96.371	
	4.4300	4.2662	96.303	
	4.6470	4.4764	96.329	
	5.8520	5.6397	96.372	

Mean, 96.316,  $\pm$  .0055

The work done by Richards† was of a much more elaborate kind, for it involved some collateral investigations as to the effect of heat upon barium chloride, etc. Every precaution was taken to secure the spectroscopic purity of the material, which was prepared from several sources, and similar care was taken with regard to the silver. For details upon these points the original paper must be consulted. As for the titrations, three methods were adopted, and a special study was made with reference to the accurate determination of the end point; in which particular the investigations of Pelouze, Marignac, and Dumas were at fault. In the first series of determinations, silver was added in excess, and the latter was measured with a standard solution of hydrochloric acid. The end point was ascertained by titrating backward and forward with silver solution and acid, and was taken as the mean between the two apparent end points thus observed. The results of this series, with weights reduced to vacuum standards, were as follows :

<i>Ag.</i>	<i>BaCl<sub>2</sub>.</i>	<i>Ratio.</i>
6.1872	5.9717	96.517
5.6580	5.4597	96.495
3.5988	3.4728	96.499
9.4010	9.0726	96.507
.7199	.6950	96.541

Mean, 96.512,  $\pm$  .0055

\*Ann. Chem. Pharm., 113, 22. 1860. Ann. Chim. Phys. (3), 55, 129.

†Proc. Amer. Acad., 29, 55. 1893.

In the second series of experiments a small excess of silver was added as before, and the precipitate of silver chloride was removed by filtration. The filtrate and wash waters were concentrated to small bulk whereupon a trace of silver chloride was obtained and taken into account. The excess of silver remaining was then thrown down as silver bromide, and from the weight of the latter the silver was calculated, and subtracted from the original amount.

<i>Ag.</i>	<i>BaCl<sub>2</sub>.</i>	<i>Ratio.</i>
6.59993	6.36974	96.512
5.55229	5.36010	96.539
4.06380	3.92244	96.522

Mean, 96.524,  $\pm .0054$

The third series involved mixing solutions of barium chloride and silver in as nearly as possible equivalent amounts, and then determining the actual quantities of silver and chlorine left unprecipitated. The filtrate and wash waters were divided into two portions, one-half being evaporated with hydrobromic acid and the other with silver nitrate. The small amounts of silver bromide and chloride thus obtained were determined by reduction and the use of Volhard's method :

<i>Ag.</i>	<i>BaCl<sub>2</sub>.</i>	<i>Ratio.</i>
4.4355	4.2815	96.528
2.7440	2.6488	96.531
6.1865	5.9712	96.520
3.4023	3.2841	96.526

Mean, 96.526,  $\pm .0035$

Two final experiments were carried out by Stas' method, somewhat as in the first series, with variations and greater refinement in the observation of the end point. The results were as follows :

<i>Ag.</i>	<i>BaCl<sub>2</sub>.</i>	<i>Ratio.</i>
6.7342	6.50022	96.525
10.6023	10.23365	96.523

Mean, 96.524,  $\pm .0007$

A careful study of Richards' paper will show that, although the last two experiments are probably the best, they are not entitled to such preponderance of weight as the "probable error" here computed would give them. I therefore treat Richards' work as I have already done that of Marignac and Dumas, regarding all of his series as one, which gives for the value of the ratio 96.520,  $\pm .0025$ . This combines with the previous series thus :

Pelouze .....	96.457, $\pm .0036$
Marignac.....	96.360, $\pm .0024$
Dumas.....	96.316, $\pm .0055$
Richards .....	96.520, $\pm .0025$
<hr/>	
General mean.....	96.434, $\pm .0015$

The ratio between silver and crystallized barium chloride has also been fixed by Marignac.\* The usual method was employed, and two series of experiments were made, in the second of which the water of crystallization was determined previous to the estimation. Five grammes of chloride were taken in each determination. The following quantities of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  correspond to 100 parts of silver :

$$\begin{array}{l} \text{A. } \left\{ \begin{array}{l} 113.109 \\ 113.135 \\ 113.097 \end{array} \right\} \text{Mean, } 113.114 \\ \text{B. } \left\{ \begin{array}{l} 113.135 \\ 113.122 \\ 113.060 \end{array} \right\} \text{Mean, } 113.106 \\ \hline \text{Mean, } 113.110, \pm .0079 \end{array}$$

The direct ratio between the chlorides of silver and barium has been measured by Berzelius. Turner, and Richards. Berzelius † found of barium chloride proportional to 100 parts of silver chloride—

$$\begin{array}{r} 72.432 \\ 72.422 \\ \hline \text{Mean, } 72.427 \end{array}$$

Turner ‡ made five experiments, with the following results :

$$\begin{array}{r} 72.754 \\ 72.406 \\ 72.622 \\ 72.664 \\ 72.653 \\ \hline \text{Mean, } 72.680, \pm .0154 \end{array}$$

Of these, Turner regards the fourth and fifth as the best ; but for present purposes it is not desirable to so discriminate.

Richards' determinations § fall into three series, and all are characterized by their taking into account chloride of silver recovered from the wash waters. In the first series the barium chloride was ignited at low redness in air or nitrogen ; in the second series it was fused in a stream of pure hydrochloric acid ; and in the third series it was not ignited at all. In the last series it was weighed in the crystallized state, and the

\* Journ. für Prakt. Chem., 74, 212. 1858.

† Poggend. Annalen, 8, 177.

‡ Phil. Trans., 1829, 291.

§ Proc. Amer. Acad., 29, 55. 1893.

amount of anhydrous chloride was computed from the data so obtained. The data, corrected to vacuum standards, are as follows:

	<i>AgCl.</i>	<i>BaCl<sub>2</sub>.</i>	<i>Ratio.</i>	
A.	{ 8.7673	6.3697	72.653	} Mean, 72.649
	{ 5.1979	3.7765	72.654	
	{ 4.9342	3.5846	72.648	
	{ 2.0765	1.5085	72.646	
	{ 4.4271	3.2163	72.650	
B.	{ 2.09750	1.52384	72.650	} Mean, 72.6563
	{ 7.37610	5.36010	72.669	
	{ 5.39906	3.92244	72.650	
C.	{ 8.2189	5.97123	72.6524	} Mean, 72.6555
	{ 4.5199	3.28410	72.6587	
<hr/>				Mean, 72.653, $\pm .0014$

If we assign Berzelius' work equal weight with that of Turner, the three series representing the ratio  $2\text{AgCl} : \text{BaCl}_2$  combine as follows:

Berzelius .....	72.427, $\pm .0154$
Turner.....	72.680, $\pm .0154$
Richards.....	72.653, $\pm .0014$
<hr/>	
General mean.....	72.650, $\pm .0014$

Incidentally to some of his other work, Marignac\* determined the percentage of water in crystallized barium chloride. Two sets of three experiments each were made, the first upon five grammes and the second upon ten grammes of salt. The following are the percentages obtained:

A.	{ 14.790	} Mean, 14.795
	{ 14.796	
	{ 14.800	
B.	{ 14.80	} Mean, 14.803
	{ 14.81	
	{ 14.80	

Mean, 14.799,  $\pm .0018$

The ratio between barium nitrate and barium sulphate has been determined only by Turner.† According to his experiments 100 parts of sulphate correspond to the following quantities of nitrate:

112.060
111.990
112.035
<hr/>

Mean, 112.028,  $\pm .014$

For the similar ratio between barium chloride and barium sulphate, there are available determinations by Turner, Berzelius, Struve, Marignac, and Richards.

\* Journ. für Prakt. Chem., 74, 312. 1858.

† Phil. Trans., 1833, 538.

Turner\* found that 100 parts of chloride ignited with sulphuric acid gave 112.19 parts of sulphate. By the common method of precipitation and filtration a lower figure was obtained, because of the slight solubility of the sulphate. This point bears directly upon many other atomic weight determinations.

Berzelius,† treating barium chloride with sulphuric acid, obtained the following results in  $\text{BaSO}_4$  for 100 parts of  $\text{BaCl}_2$ :

	112.17
	112.18
	<hr/>
Mean,	112.175

Struve,‡ in two experiments, found:

	112.0912
	112.0964
	<hr/>
Mean,	112.0938

Marignac's§ three results are as follows:

8.520 grm. $\text{BaCl}_2$ gave	9.543 $\text{BaSO}_4$ .	Ratio,	112.007
8.519	" 9.544	"	112.032
8.520	" 9.542	"	111.995
			<hr/>
		Mean,	112.011, $\pm .0071$

Richards, in his work on this ratio, regards the results as of slight value, because of the occlusion of the chloride by the sulphate. This source of error he was never able to avoid entirely. Another error in the opposite direction is found in the retention of sulphuric acid by the precipitated sulphate. Eight experiments were made in two series, one set by adding sulphuric acid to a strong solution of barium chloride in a platinum crucible, the other by precipitation in the usual way. Richards gives in his published paper only the end results and the mean of his determinations; the details cited below I owe to his personal kindness. The weights are reduced to vacuum standards:

	$\text{BaCl}_2$ .	$\text{BaSO}_4$ .	Ratio.
First.	{ 1.78934	2.0056	112.086
	{ 2.07670	2.3274	112.072
	{ 1.58311	1.7741	112.064
	{ 3.27563	3.6712	112.076
	{ 3.02489	3.3903	112.080
	{ 3.87091	4.3385	112.080
Second.	{ 3.02489	3.9726	112.076
	{ 3.87091	3.4880	112.085
			<hr/>
		Mean,	112.077, $\pm .0017$

\* Phil. Trans., 1829, 291.

† Poggend. Annalen, 8, 177.

‡ Ann. Chem. Pharm., 80, 204. 1851.

§ Journ. für Prakt. Chem., 74, 212. 1858.

This mean is subject to a small correction due to loss of chlorine on drying the chloride, which reduces it to 112.073. Omitting Turner's single determination as unimportant, and assigning to the work of Berzelius and of Struve equal weight with that of Marignac, the measurements of this ratio combine thus:

Berzelius .....	112.175, $\pm$ .0071
Struve .....	112.094, $\pm$ .0071
Marignac.....	112.011, $\pm$ .0071
Richards .....	112.073, $\pm$ .0017
General mean.....	112.075, $\pm$ .0016

In an earlier paper than the one previously cited, Richards\* studied with great care the ratios connecting barium bromide with silver and silver bromide. The barium bromide was prepared by several distinct processes, its behavior upon dehydration and even upon fusion was studied, and its specific gravity was determined. The ratio with silver was measured by titration, a solution of hydrobromic acid being used for titrating back. The data are subjoined, with the  $\text{BaBr}_2$  equivalent to 100 parts of silver stated:

<i>BaBr<sub>2</sub>.</i>	<i>Ag.</i>	<i>Ratio.</i>
2.28760	1.66074	137.746
3.47120	2.52019	137.736
2.19940	1.59687	137.732
2.35971	1.71323	137.735
2.94207	2.13584	137.748
1.61191	1.17020	137.747
2.10633	1.52921	137.740
2.19682	2.11740	137.755
2.37290	1.72276	137.738
1.84822	1.34175	137.747
5.66647	4.11360	137.750
3.52670	2.56010	137.756
4.31690	3.13430	137.731
3.36635	2.44385	137.748
3.46347	2.51415	137.759

Mean, 137.745,  $\pm$  .0015

The silver bromide in most of these determinations, and in some others, was collected and weighed in a Gooch crucible with all necessary precautions. Vacuum standards were used throughout for both ratios. I give in a third column the  $\text{BaBr}_2$  equivalent to 100 parts of  $\text{AgBr}$ :



<i>BaBr<sub>2</sub>.</i>	<i>AgBr.</i>	<i>Ratio.</i>
2.28760	2.89026	79.149
3.47120	4.38635	79.136
3.81086	4.81688	79.133
2.35971	2.98230	79.124
2.94207	3.71809	79.129
2.10633	2.66191	79.128
2.91682	3.68615	79.129
2.37290	2.99868	79.131
1.84822	2.33530	79.143
1.90460	2.40733	79.116
5.66647	7.16120	79.127
3.52670	4.45670	79.133
2.87743	3.63644	79.127
3.46347	4.37669	79.135

Mean, 79.132,  $\pm$  .0015

The ratios for barium now sum up as follows:

- (1.)  $\text{Ag}_2 : \text{BaCl}_2 :: 100 : 96.434, \pm .0015$
- (2.)  $\text{Ag}_2 : \text{BaCl}_2.2\text{H}_2\text{O} :: 100 : 113.110, \pm .0079$
- (3.)  $2\text{AgCl} : \text{BaCl}_2 :: 100 : 72.650, \pm .0014$
- (4.) Per cent. of  $\text{H}_2\text{O}$  in  $\text{BaCl}_2.2\text{H}_2\text{O}$ , 14.799,  $\pm .0018$
- (5.)  $\text{BaSO}_4 : \text{BaN}_2\text{O}_6 :: 100 : 112.028, \pm .014$
- (6.)  $\text{BaCl}_2 : \text{BaSO}_4 :: 100 : 112.075, \pm .0016$
- (7.)  $\text{Ag}_2 : \text{BaBr}_2 :: 100 : 137.745, \pm .0015$
- (8.)  $2\text{AgBr} : \text{BaBr}_2 :: 100 : 79.132, \pm .0015$

The reduction of these ratios depends upon the subjoined antecedent values:

Ag = 107.108, $\pm$ .0031	N = 13.935, $\pm$ .0021
Cl = 35.179, $\pm$ .0048	S = 31.828, $\pm$ .0015
Br = 79.344, $\pm$ .0062	AgCl = 142.287, $\pm$ .0037
O = 15.879, $\pm$ .0003	AgBr = 186.452, $\pm$ .0054

With these factors four estimates are obtainable for the molecular weight of barium chloride:

From (1).....	$\text{BaCl}_2 = 206.577, \pm .0068$
From (2).....	" = 206.542, $\pm .0183$
From (3).....	" = 206.745, $\pm .0067$
From (4).....	" = 205.866, $\pm .0257$
General mean.....	$\text{BaCl}_2 = 206.629, \pm .0045$

For barium bromide we have:

From (7).....	$\text{BaBr}_2 = 295.070, \pm .0091$
From (8).....	" = 295.086, $\pm .0102$
General mean.....	$\text{BaBr}_2 = 295.078, \pm .0068$

And for barium itself, four values are finally available, thus :

From molecular weight $\text{BaCl}_2$ .....	$\text{Ba} = 136.271, \pm .0106$
From molecular weight $\text{BaBr}_2$ .....	" = $136.390, \pm .0141$
From ratio (5) .....	" = $135.600, \pm .2711$
From ratio (6) .....	" = $136.563, \pm .0946$
General mean.....	$\text{Ba} = 136.315, \pm .0085$

Or, if  $\text{O} = 16$ ,  $\text{Ba} = 137.354$ .

In the foregoing computation all the data, good or bad, are included. Some of them, as shown by the weights, practically vanish ; but others, as in the chloride series, carry an undue influence. A more trustworthy result can be deduced from Richards' experiments alone, which reduce as follows :

From $\text{Ag}_2 : \text{BaCl}_2$ .....	$\text{BaCl}_2 = 206.761, \pm .0080$
From $2\text{AgCl} : \text{BaCl}_2$ .....	" = $206.754, \pm .0067$
General mean.....	$\text{BaCl}_2 = 206.755, \pm .0051$

From the bromide, as given above,  $\text{Ba} = 136.390, \pm .0141$ . From the value just found for the chloride,  $\text{Ba} = 136.397, \pm .0109$ . Combining the two values—

$$\text{Ba} = 136.392, \pm .0086.$$

Or, if  $\text{O} = 16$ ,  $\text{Ba} = 137.434$ . This determination will be adopted in subsequent calculations as the most probable.

## LEAD.

For the atomic weight of lead we have to consider experiments made upon the oxide, chloride, nitrate, and sulphate. The researches of Berzelius upon the carbonate and various organic salts need not now be considered, nor is it worth while to take into account any work of his done before the year 1818. The results obtained by Döbereiner\* and by Longchamp† are also without special present value.

For the exact composition of lead oxide we have to depend upon the researches of Berzelius. His experiments were made at different times through quite a number of years; but were finally summed up in the last edition of his famous "Lehrbuch."‡ In general terms his method of experiment was very simple. Perfectly pure lead oxide was heated in a current of hydrogen, and the reduced metal weighed. From his weighings I have calculated the percentages of lead thus found and given them in a third column:

*Earlier Results.*

8.045	gram. PbO gave	7.4675	gram. Pb.	92.8217	per cent.
14.183	"	13.165	"	92.8224	"
10.8645	"	10.084	"	92.8160	"
13.1465	"	12.2045	"	92.8346	"
21.9425	"	20.3695	"	92.8313	"
11.159	"	10.359	"	92.8309	"

*Latest.*

6.6155	"	6.141	"	92.8275	"
14.487	"	13.448	"	92.8280	"
14.626	"	13.5775	"	92.8313	"

Mean, 92.8271,  $\pm .0013$

For the synthesis of lead sulphate we have data by Berzelius, Turner, and Stas. Berzelius,§ whose experiments were intended rather to fix the atomic weight of sulphur, dissolved in each estimation ten grammes of pure lead in nitric acid, then treated the resulting nitrate with sulphuric acid, brought the sulphate thus formed to dryness, and weighed. One hundred parts of metal yield of  $\text{PbSO}_4$ :

146.380
146.400
146.440
146.458

Mean, 146.419,  $\pm .012$

\* Schweig. Journ., 17, 241. 1816.

† Ann. Chim. Phys., 34, 105. 1827.

‡ Bd. 3, s. 1218.

§ Lehrbuch, 5th ed., 3, 1187.

Turner,\* in three similar experiments, found as follows :

146.430
146.398
146.375
<hr/>
Mean, 146.401, $\pm .011$

In these results of Turner's, *absolute* weights are implied.

The results of Stas' syntheses,† effected after the same general method, but with variations in details, are as follows. Corrections for weighing in air were applied :

146.443
146.427
146.419
146.432
146.421
146.423
<hr/>
Mean, 146.4275, $\pm .0024$

Combining, we get the subjoined result:

Berzelius.....	146.419, $\pm .012$
Turner.....	146.401, $\pm .011$
Stas.....	146.4275, $\pm .0024$
	<hr/>
General mean.....	146.4262, $\pm .0023$

Turner, in the same paper, also gives a series of syntheses of lead sulphate, in which he starts from the oxide instead of from the metal. One hundred parts of PbO, upon conversion into PbSO<sub>4</sub>, gained weight as follows :

35.84
35.71
35.84
35.75
35.79
35.78
35.92
<hr/>
Mean, 35.804, $\pm .018$

These figures are not wholly reliable. Numbers one, two, and three represent lead oxide contaminated with traces of nitrate. The oxide of four, five, and six contained traces of minium. Number seven was free from these sources of error, and, therefore, deserves more consideration. The series as a whole undoubtedly gives too low a figure, and this error would tend to slightly raise the atomic weight of lead.

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\* Phil. Trans., 1833, 527-538.

† Aronstein's translation, 333.

Still a third series by Turner establishes the ratio between the nitrate and the sulphate, a known weight of the former being in each experiment converted into the latter. One hundred parts of sulphate represent of nitrate:

109.312
109.310
109.300
<hr/>
Mean, 109.307, $\pm .002$

In all these experiments by Turner the necessary corrections were made for weighing in air.

In 1846 Marignac\* published two sets of determinations of only moderate value. First, chlorine was conducted over weighed lead, and the amount of chloride so formed was determined. The lead chloride was fused before weighing. The ratio to 100 Pb is given in the last column:

20.506	gram. Pb gave	27.517	PbCl <sub>2</sub> .	134.190
16.281	"	21.858	"	134.225
25.454	"	34.149	"	134.159
				<hr/>
				Mean, 134.191, $\pm .013$

Secondly, lead chloride was precipitated by silver nitrate and the ratio between PbCl<sub>2</sub> and 2AgCl determined. The third column gives the AgCl formed by 100 parts of PbCl<sub>2</sub>:

12.534	gram. PbCl <sub>2</sub> gave	12.911	AgCl.	103.01
14.052	"	14.506	"	103.23
25.533	"	26.399	"	103.39
				<hr/>
				Mean, 103.21, $\pm .0745$

For the ratio between lead chloride and silver we have a series of results by Marignac and one experiment by Dumas. There are also unavailable data by Turner and by Berzelius.

Marignac,† applying the method used in his researches upon barium and strontium, and working with lead chloride which had been dried at 200°, obtained these results. The third column gives the ratio between PbCl<sub>2</sub>, and 100 parts of Ag:

4.9975	gram. PbCl <sub>2</sub> =	3.8810	gram. Ag.	128.768
4.9980	"	3.8835	"	128.698
5.0000	"	3.8835	"	128.750
5.0000	"	3.8860	"	128.667
				<hr/>
				Mean, 128.721, $\pm .016$

Dumas,‡ in his investigations, found that lead chloride retains traces

\* Ann. Chem. Pharm., 59, 289, and 290. 1846.

† Journ. für Prakt. Chem., 74, 218. 1858.

‡ Ann. Chem. Pharm., 113, 35. 1860.

of water even at  $250^{\circ}$ , and is sometimes also contaminated with oxychloride. In one estimation 8.700 grammes  $\text{PbCl}_2$  saturated 6.750 of Ag. The chloride contained .009 of impurity; hence, correcting,  $\text{Ag} : \text{PbCl}_2 :: 100 : 128.750$ . If we assign this figure equal weight with those of Marignac, we get as the mean of all  $128.7266, \pm .013$ . The sources of error indicated by Dumas, if they are really involved in this mean, would tend slightly to raise the atomic weight of lead.

The synthesis of lead nitrate, as carried out by Stas,\* gives excellent results. Two series of experiments were made, with from 103 to 250 grammes of lead in each determination. The metal was dissolved in nitric acid, the solution evaporated to dryness with extreme care, and the nitrate weighed. All weighings were reduced to the vacuum standard. In series A the lead nitrate was dried in an air current at a temperature of about  $155^{\circ}$ . In series B the drying was effected in vacuo. 100 of lead yield of nitrate :

## A.

159.973

159.975

159.982

159.975

159.968

159.973

---

 Mean, 159.9743,  $\pm .0012$ 

## B.

159.970

159.964

159.959

159.965

---

 Mean, 159.9645,  $\pm .0015$ 

 Mean from both series, 159.9704,  $\pm .0010$ 

There is still another set of experiments upon lead nitrate, originally intended to fix the atomic weight of nitrogen, which may properly be included here. It was carried out by Anderson† in Svanberg's laboratory, and has also appeared under Svanberg's name. Lead nitrate was carefully ignited, and the residual oxide weighed, with the following results :

5.19485	grm. $\text{PbN}_2\text{O}_6$	gave	3.5017	grm. $\text{PbO}$ .	67.4071	per cent.
9.7244	"		6.5546	"	67.4037	"
9.2181	"		6.2134	"	67.4044	"
9.6530	"		6.5057	"	67.3957	"

---

 Mean, 67.4027,  $\pm .0016$ 


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 \* Aronstein's translation, 316.

† Ann. Chim. Phys. (3), 9, 254. 1843.

We have now nine ratios from which to compute:

- (1.) Per cent. of Pb in PbO, 92.8271,  $\pm .0013$
- (2.) Per cent of PbO in  $\text{PbN}_2\text{O}_6$ , 67.4027,  $\pm .0016$
- (3.) Pb :  $\text{PbSO}_4$  :: 100 : 146.4262,  $\pm .0023$
- (4.) PbO :  $\text{PbSO}_4$  :: 100 : 135.804,  $\pm .0180$
- (5.)  $\text{PbSO}_4$  :  $\text{PbN}_2\text{O}_6$  :: 100 : 109.307,  $\pm .0020$
- (6.) Pb :  $\text{PbN}_2\text{O}_6$  :: 100 : 159.9704,  $\pm .0010$
- (7.) Pb :  $\text{PbCl}_2$  :: 100 : 134.191,  $\pm .013$
- (8.)  $\text{PbCl}_2$  :  $2\text{AgCl}$  :: 100 : 103.21,  $\pm .0745$
- (9.)  $\text{Ag}_2$  :  $\text{PbCl}_2$  :: 100 : 128.7266,  $\pm .0130$

To reduce these ratios we must use the following data :

O = 15.879, $\pm .0003$	S = 31.828, $\pm .0015$
Ag = 107.108, $\pm .0031$	N = 13.935, $\pm .0021$
Cl = 35.179, $\pm .0048$	AgCl = 142.287, $\pm .0037$

For the molecular weight of lead oxide we now get three estimates :

From (1) .....	PbO = 221.375, $\pm .0403$
From (2) .....	" = 221.796, $\pm .0132$
From (4) .....	" = 221.944, $\pm .1116$
<hr/>	
General mean .....	PbO = 221.757, $\pm .0125$

For lead chloride we have—

From (8) ....	$\text{PbCl}_2$ = 275.723, $\pm .1989$
From (9) ....	" = 275.753, $\pm .0290$
<hr/>	
General mean .....	$\text{PbCl}_2$ = 275.752, $\pm .0287$

Including these results, six values are calculable for the atomic weight of lead :

From molecular weight of PbO .....	Pb = 205.878, $\pm .0126$
From molecular weight of $\text{PbCl}_2$ .....	" = 205.394, $\pm .0302$
From (3) .....	" = 205.367, $\pm .0051$
From (5) .....	" = 203.352, $\pm .0479$
From (6) .....	" = 205.341, $\pm .0068$
From (7) .....	" = 205.779, $\pm .0831$
<hr/>	
General mean .....	Pb = 205.395, $\pm .0038$

If  $\text{O} = 16$ ,  $\text{Pb} = 206.960$ . If we reject the first, fourth, and sixth of these values, which are untrustworthy, the remaining second, third, and fifth give a general mean of  $\text{Pb} = 205.358, \pm .0040$ . If  $\text{O} = 16$ , this becomes  $\text{Pb} = 206.923$ . From Stas' ratios alone Stas calculates  $\text{Pb} = 206.918$  to  $206.934$ ; Ostwald finds  $206.911$ ; Van der Plaats (A),  $206.9089$ , (B),  $206.9308$ , and Thomsen  $206.9042$ . The value adopted here represents mainly the work of Stas, and with  $\text{H} = 1$  is

$$\text{Pb} = 205.358, \pm .0040.$$

## GLUCINUM.

Our knowledge of the atomic weight of glucinum is chiefly derived from experiments made upon the sulphate. Leaving out of account the single determination by Berzelius,\* we have to consider the data furnished by Awdejew, Weeren, Klatzo, Debray, Nilson and Pettersson, and Kriess and Moraht.

Awdejew, † whose determination was the earliest of any value, analyzed the sulphate. The sulphuric acid was thrown down as barium sulphate; and in the filtrate, from which the excess of barium had been first removed, the glucina was precipitated by ammonia. The figures which Awdejew publishes represent the ratio between  $\text{SO}_3$  and  $\text{GLO}$ , but not absolute weights. As, however, his calculations were made with  $\text{SO}_3 = 501.165$ , and  $\text{Ba}$  probably  $= 855.29$ , we may add a third column showing how much  $\text{BaSO}_4$  is proportional to 100 parts of  $\text{GLO}$ :

$\text{SO}_3$ .	$\text{GLO}$ .	<i>Ratio.</i>
4457	1406	921.242
4531	1420	927.304
7816	2480	915.903
12880	4065	920.814

Mean, 921.316,  $\pm 1.577$

The same method was followed by Weeren and by Klatzo, except that Weeren used ammonium sulphide instead of ammonia for the precipitation of the glucina. Weeren ‡ gives the following weights of  $\text{GLO}$  and  $\text{BaSO}_4$ . The ratio is given in a third column, just as with the figures by Awdejew:

$\text{GLO}$ .	$\text{BaSO}_4$ .	<i>Ratio.</i>
.3163	2.9332	927.031
.2872	2.6377	918.419
.2954	2.7342	925.592
.5284	4.8823	902.946

Mean, 918.497,  $\pm 3.624$

Klatzo's § figures are as follows, with the third column added by the writer:

$\text{GLO}$ .	$\text{BaSO}_4$ .	<i>Ratio.</i>
.2339	2.1520	920.052
.1910	1.7556	919.162
.2673	2.4872	930.490
.3585	3.3115	923.710
.2800	2.5842	922.989

Mean, 923.281,  $\pm 1.346$

\* Poggend. *Annal.*, 8, 1.

† Poggend. *Annal.*, 56, 106. 1842.

‡ Poggend. *Annal.*, 92, 124. 1854.

§ *Zeitschr. Anal. Chem.*, 8, 523. 1869.



Combining these series into a general mean, we get the subjoined result :

Awdejew.....	921.316, $\pm$ 1.577
Weeren.....	918.497, $\pm$ 3.624
Klatzo.....	923.281, $\pm$ 1.346
General mean.....	922.164, $\pm$ 0.985

Hence  $\text{GLO} = 25.130, \pm .0269$ .

Debray\* analyzed a double oxalate of glucinum and ammonium,  $\text{Gl}(\text{NH}_4)_2\text{C}_4\text{O}_8$ . In this the glucina was estimated by calcination, after first converting the salt into nitrate. The following percentages were found :

11.5
11.2
11.6
Mean, 11.433, $\pm$ .081

The carbon was estimated by an organic combustion. I give the weights, and put in a third column the percentages of  $\text{CO}_2$  thus obtained :

<i>Salt.</i>	<i>CO<sub>2</sub>.</i>	<i>Per cent. CO<sub>2</sub>.</i>
.600	.477	79.500
.603	.478	79.270
.600	.477	79.500
Mean, 79.423, $\pm$ .052		

Calculating the ratio between  $\text{CO}_2$  and  $\text{GLO}$ , we have for the molecular weight of the latter,  $\text{GLO} = 25.151, \pm .1783$ .

In 1880 the careful determinations of Nilson and Pettersson appeared.† These chemists first attempted to work with the sublimed chloride of glucinum, but abandoned the method upon finding the compound to be contaminated with traces of lime derived from a glass tube. They finally resorted to the crystallized sulphate as the most available salt for their purposes. This compound, upon strong ignition, yields pure glucina. The data are as follows :

<i>GlSO<sub>4</sub>.4H<sub>2</sub>O.</i>	<i>GLO.</i>	<i>Per cent. GLO.</i>
3.8014	.5387	14.171
2.6092	.3697	14.169
4.3072	.6099	14.160
3.0091	.4266	14.176
Mean, 14.169, $\pm$ .0023		

Krüss and Moraht‡ in their work follow the general method adopted

\* Ann. Chim. Phys. (3), 44, 37. 1855.

† Berichte d. Deutsch. Chem. Gesell., 13, 1451. 1880.

‡ Ann. d. Chem., 262, 38. 1891.

by Nilson and Pettersson, but with various added precautions and greater elaboration of detail. Their glucina was derived from three sources, namely, leucophane, beryl, and gadolinite, and the sulphate was repeatedly recrystallized. The results are subjoined:

$GlSO_4 \cdot 4H_2O$ .	$GlO$ .	<i>Per cent. GlO.</i>
21.1928	3.0008	14.160
16.2038	2.29455	14.161
15.49345	2.1902	14.136
20.1036	2.8433	14.143
22.0465	3.1167	14.137
4.9619	.7019	14.146
18.3249	2.5921	14.145
24.3907	3.0253	14.143
20.18045	2.85255	14.135
20.0253	2.8328	14.146
18.9840	2.6832	14.134
17.0072	2.4073	14.155
22.5044	3.1805	14.133
20.88675	2.95645	14.154
19.0591	2.69305	14.130
17.8227	2.5226	14.153

Mean, 14.144,  $\pm$  .0017

The first two determinations, which give the highest percentage, were made upon sulphate thrice crystallized. The others were made upon a salt four times crystallized, except in one instance, when there were five crystallizations. To the data derived from the four times crystallized compound Krüss and Moraht give preference, and so find a slightly lower value for the atomic weight of glucinum. Combining, we have for the mean percentage:

By Nilson and Pettersson . . . . .	14.169, $\pm$ .0023
By Krüss and Moraht . . . . .	14.144, $\pm$ .0017
General mean . . . . .	14.153, $\pm$ .0014

Taking now all the data for glucinum, we have—

- (1.)  $GlO : BaSO_4 :: 100 : 922.164, \pm .985$
- (2.)  $4CO_2 : GlO :: 79.423, \pm .0052 : 11.433, \pm .081$
- (3.) Percentage of  $GlO$  in  $GlSO_4 \cdot 4H_2O$ , 14.153,  $\pm$  .0014

The antecedent atomic weights are—

O = 15.879, $\pm$ .0003	C = 11.920, $\pm$ .0004
S = 31.828, $\pm$ .0015	Ba = 136.392, $\pm$ .0086

Hence the subjoined values for glucina :

From (1).....	G1O = 25.130, $\pm$ .0269
From (2).....	" = 25.151, $\pm$ .1783
From (3).....	" = 24.891, $\pm$ .0025
<hr/>	
General mean.....	G1O = 24.893, $\pm$ .0025
	And G1 = 9.014, $\pm$ .0025

If O = 16, G1 = 9.083.

All the values but that derived from the third ratio might obviously be rejected. Their influence upon the final mean is altogether trivial.

## MAGNESIUM.

There is perhaps no common metal of which the atomic weight has been subjected to closer scrutiny than that of magnesium. The value is low, and its determination should, therefore, be relatively free from many of the ordinary sources of error ; it is extensively applied in chemical analysis, and ought consequently to be accurately ascertained. Strange discrepancies, however, exist between the results obtained by different investigators ; so that the generally accepted figure cannot be regarded as absolutely free from doubt.

The early determinations made by Berzelius, Longchamp, and Gay-Lussac need not be considered here, as they have only antiquarian value. The investigations which demand attention are those of Scheerer, Svanberg and Nordenfeldt, Jacquelin, Macdonnell, Bahr, Marchand and Scheerer, Dumas, Marignac, Burton and Vorce, and Richards and Parker.

Scheerer's method of investigation was exceedingly simple.\* He merely estimated the sulphuric acid in anhydrous magnesium sulphate, employing the usual process of precipitation as barium sulphate. He gives no weighings, but reports the percentages of  $\text{SO}_3$  thus found. In his calculations, O = 100,  $\text{SO}_3$  = 500.75, and BaO = 955.29. It is easy, therefore, to recalculate the figures which he gives, so as to establish what his method really represents, viz., the ratio between the sulphates of barium and magnesium.

Thus revised, his four analyses show that 100 parts of  $\text{MgSO}_4$  yield the following quantities of  $\text{BaSO}_4$  :

	<i>Per cent. <math>\text{SO}_3</math>.</i>
193.575	66.573
193.677	66.608
193.767	66.639
193.631	66.592
<hr/>	
Mean, 193.6625, $\pm$ .0274	

\* Poggend. Annalen, 69, 535. 1846.

In a later note\* Scheerer shows that the barium sulphate of these experiments carries down with it magnesium salts in such quantity as to make the atomic weight of magnesium 0.039 too low.

The work of Bahr, Jacquelain, Macdonnell, and Marignac, and in part that of Svanberg and Nordenfeldt, also relates to the composition of magnesium sulphate.

Jacquelain's experiments were as follows: † Dry magnesium sulphate was prepared by mixing the ordinary hydrous salt to a paste with sulphuric acid, and calcining the mass in a platinum crucible over a spirit lamp to constant weight and complete neutrality of reaction. This dry sulphate was weighed and intensely ignited three successive times. The weight of the residual MgO having been determined, it was moistened with sulphuric acid and recalcined over a spirit lamp, thus reproducing the original weight of  $\text{MgSO}_4$ . Jacquelain's weighings for these two experiments show that 100 parts of MgO correspond to the quantities of  $\text{MgSO}_4$  given in the last column:

1.466 grm. $\text{MgSO}_4$ gave	.492 grm. MgO.	297.968
.492 " MgO " 1.466 " $\text{MgSO}_4$ .		297.968

Jacquelain\* also made one estimation of sulphuric acid in the foregoing sulphate as  $\text{BaSO}_4$ . His result (1.464 grm.  $\text{MgSO}_4 = 2.838$  grm.  $\text{BaSO}_4$ ), reduced to the standard adopted in dealing with Scheerer's experiments, gives for 100 parts of  $\text{MgSO}_4$ , 193.852  $\text{BaSO}_4$ . If this figure be given equal weight with a single experiment in Scheerer's series, and combined with the latter, the mean will be 193.700,  $\pm .0331$ . This again is subject to the correction pointed out by Scheerer for magnesium salts retained by the barium sulphate, but such a correction determined by Scheerer for a single experiment is only a rough approximation, and hardly worth applying.

The determinations published by Macdonnell ‡ are of slight importance, and all depend upon magnesium sulphate. First, the crystallized salt,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , was dried in vacuo over sulphuric acid and then dehydrated at a low red heat. The following percentages of water were found:

51.17
51.13
51.14
51.26
51.28
51.29
—

Mean, 51.21,  $\pm .020$

\* Poggend. Annalen, 70, 407.

† Ann. Chim. Phys. (3), 32, 202.

‡ Proc. Royal Irish Acad., 5, 303. British Association Report, 1852, part 2, p. 36.

Secondly, anhydrous magnesium sulphate was precipitated with barium chloride. From the weight of the barium sulphate, with  $\text{SO}_3 = 80$  and  $\text{Ba} = 137$ , Macdonnell computes the percentages of  $\text{SO}_3$  given below. I calculate them back to the observed ratio in uniformity with Scheerer's work :

<i>Per cent. <math>\text{SO}_3</math>.</i>	<i>Ratio, <math>\text{MgSO}_4 : \text{BaSO}_4</math>.</i>
66.67	194.177
66.73	194.351
66.64	194.089
66.65	194.118
66.69	194.239

In another experiment 60.05 grains  $\text{MgSO}_4$  gave 116.65 grains  $\text{BaSO}_4$ , a ratio of 100 : 194.254. Including this with the preceding figures, they give a mean of 194.205,  $\pm .027$ . This, combined with the work of Scheerer and Jacquelin, 193.700,  $\pm .033$ , gives a general mean of—

$$\text{MgSO}_4 : \text{BaSO}_4 :: 100 : 194.003, \pm .021.$$

In one final experiment Macdonnell found that 41.44 grains of pure magnesia gave 124.40 grains of  $\text{MgSO}_4$ , or 300.193 per cent.

Bahr's\* work resembles in part that of Jacquelin. This chemist converted pure magnesium oxide into sulphate, and from the increase in weight determined the composition of the latter salt. From his weighings 100 parts of  $\text{MgO}$  equal the amounts of  $\text{MgSO}_4$  given in the third column :

1.6938	gram. $\text{MgO}$ gave	5.0157	gram. $\text{MgSO}_4$ .	296.122
2.0459	“	6.0648	“	296.437
1.0784	“	3.1925	“	296.040
				Mean, 296.200, $\pm .0815$

About four years previous to the investigations of Bahr the paper of Svanberg and Nordenfeldt† appeared. These chemists started with the oxalate of magnesium, which was dried at a temperature of from  $100^\circ$  to  $105^\circ$  until it no longer lost weight. The salt then contained two molecules of water, and upon strong ignition it left a residue of  $\text{MgO}$ . The percentage of  $\text{MgO}$  in the oxalate comes out as follows :

7.2634	gram. oxalate gave	1.9872	gram. oxide.	27.359	per cent.
6.3795	“	1.7464	“	27.375	“
6.3653	“	1.7418	“	27.364	“
6.2216	“	1.7027	“	27.368	“
				Mean, 27.3665, $\pm .0023$	

\* Journ. für Prakt. Chem., 56, 310. 1852.

† Journ. für Prakt. Chem., 45, 473. 1848.

In three of these experiments the  $\text{MgO}$  was treated with  $\text{H}_2\text{SO}_4$ , and converted, as by Jacquelin and by Bahr in their later researches, into  $\text{MgSO}_4$ . One hundred parts of  $\text{MgO}$  gave of  $\text{MgSO}_4$  as follows :

1.9872 grm.	$\text{MgO}$ gave	5.8995 grm.	$\text{MgSO}_4$ .	296.875
1.7464	"	5.1783	"	296.513
1.7418	"	5.1666	"	296.624

Mean, 296.671,  $\pm .072$

In 1850 the elaborate investigations of Marchand and Scheerer\* appeared. These chemists undertook to determine the composition of some natural magnesites, and, by applying corrections for impurities, to deduce from their results the sought-for atomic weight. The magnesite chosen for the investigation was, first, a yellow, transparent variety from Snarum; second, a white opaque mineral from the same locality; and, third, a very pure quality from Frankenstein. In each case the impurities were carefully determined; but only a part of the details need be cited here. Silica was of course easily corrected for by simple subtraction from the sum of all of the constituents; but iron and calcium, when found, having been present in the mineral as carbonates, required the assignment to them of a portion of the carbonic acid. In the atomic weight determinations the mineral was first dried at  $300^\circ$ . The loss in weight upon ignition was then carbon dioxide. It was found, however, that even here a correction was necessary. Magnesite, upon drying at  $300^\circ$ , loses a trace of  $\text{CO}_2$ , and still retains a little water; on the other hand, a minute quantity of  $\text{CO}_2$  remains even after ignition. The  $\text{CO}_2$  expelled at  $300^\circ$  amounted in one experiment to .054 per cent.; that retained after calcination to .055 per cent. Both errors tend in the same direction, and increase the apparent percentage of  $\text{MgO}$  in the magnesite. On the yellow mineral from Snarum the crude results are as follows, giving percentages of  $\text{MgO}$ ,  $\text{FeO}$ , and  $\text{CO}_2$  after eliminating silica :

$\text{CO}_2$ .	$\text{MgO}$ .	$\text{FeO}$ .
51.8958	47.3278	.7764
51.8798	47.3393	.7809
51.8734	47.3154	.8112
51.8875	47.3372	.7753

Mean, 47.3299,  $\pm .0037$

After applying corrections for loss and retention of  $\text{CO}_2$ , as previously indicated, the mean results of the foregoing series become—

$\text{CO}_2$ .	$\text{MgO}$ .	$\text{FeO}$ .
51.9931	47.2743	.7860

The ratio between the  $\text{MgO}$  and the  $\text{CO}_2$ , after correcting for the iron, will be considered further on.

\* Journ. für Prakt. Chem., 50, 385.

Of the white magnesite from Snarum but a single analysis was made, which for present purposes may be ignored. Concerning the Frankenstein mineral three series of analyses were executed. In the first series the following results were obtained :

8.996	gram.	CO <sub>2</sub> = 8.2245	gram.	MgO.	47.760	per cent.	MgO.
7.960	"	7.2775	"	"	47.761	"	"
9.3265	"	8.529	"	"	47.767	"	"
7.553	"	6.9095	"	"	47.775	"	"
<hr/>							
Mean, 47.766, $\pm$ .0022							

This mean, corrected for loss of CO<sub>2</sub> in drying, becomes 47.681. I give series second with corrections applied :

6.8195	gram.	MgCO <sub>3</sub> gave	3.2500	gram.	MgO.	47.658	per cent.
11.3061	"	"	5.3849	"	"	47.628	"
9.7375	"	"	4.635	"	"	47.599	"
12.3887	"	"	5.9033	"	"	47.650	"
32.4148	"	"	15.453	"	"	47.674	"
38.8912	"	"	18.5366	"	"	47.663	"
26.5223	"	"	12.6445	"	"	47.675	"
<hr/>							
Mean, 47.650, $\pm$ .0069							

The third series was made upon very pure material, so that the corrections, although applied, were less influential. The results were as follows :

4.2913	gram.	MgCO <sub>3</sub> gave	2.0436	gram.	MgO.	47.622	per cent.
27.8286	"	"	13.2539	"	"	47.627	"
14.6192	"	"	6.9692	"	"	47.672	"
18.3085	"	"	8.7237	"	"	47.648	"
<hr/>							
Mean, 47.642, $\pm$ .0077							

In a supplementary paper\* by Scheerer, it was shown that an important correction to the foregoing data had been overlooked. Scheerer, re-examining the magnesites in question, discovered in them traces of lime, which had escaped notice in the original analyses. With this correction the two magnesites in question exhibit the following mean composition :

	<i>Snarum.</i>	<i>Frankenstein.</i>
CO <sub>2</sub> .....	52.131	52.338
MgO.....	46.663	47.437
CaO.....	.430	.225
FeO.....	.776	.....
	<hr/>	<hr/>
	100.000	100.000

Correcting for lime and iron, by assigning each its share of CO<sub>2</sub>, the Snarum magnesite gives as the true percentage of magnesia in pure

\* Ann. d. Chem. und Pharm., 110, 240.

magnesium carbonate, the figure 47.624. To this, without serious mistake, we may assign the weight indicated by the probable error,  $\pm .0037$ , the quantity previously deduced from the percentages of MgO given in the uncorrected analyses.

From the Frankenstein mineral, similarly corrected, the final mean percentage of MgO in  $\text{MgCO}_3$  becomes 47.628. This, however, represents three series of analyses, whose combined probable errors may be properly assigned to it. The combination is as follows:

$$\begin{array}{r} \pm .0022 \\ \pm .0069 \\ \pm .0077 \\ \hline \end{array}$$

Result,  $\pm .0020$ , probable error of the general mean.

We may now combine the results obtained from both magnesites:

Snarum mineral.....	Per cent. MgO, 47.624, $\pm .0037$
Frankenstein mineral.....	“ 47.628, $\pm .0020$
General mean.....	Per cent. MgO, 47.627, $\pm .0018$

The next investigation upon the atomic weight of magnesium which we have to consider is that of Dumas.\* Pure magnesium chloride was placed in a boat of platinum, and ignited in a stream of dry hydrochloric acid gas. The excess of the latter having been expelled by a current of dry carbon dioxide, the platinum boat, still warm, was placed in a closed vessel and weighed therein. After weighing, the chloride was dissolved and titrated in the usual manner with a solution containing a known quantity of pure silver. The weighings which Dumas reports give, as proportional to 100 parts of silver, the quantities of  $\text{MgCl}_2$  stated in the third column:

2.203	gm.	$\text{MgCl}_2 = 4.964$	gm.	Ag.	44.380
2.5215	“	5.678	“	“	44.408
2.363	“	5.325	“	“	44.376
3.994	“	9.012	“	“	44.319
2.578	“	5.834	“	“	44.189
2.872	“	6.502	“	“	44.171
2.080	“	4.710	“	“	44.161
2.214	“	5.002	“	“	44.262
2.086	“	4.722	“	“	44.176
1.688	“	3.823	“	“	44.154
1.342	“	3.031	“	“	44.276

Mean, 44.261,  $\pm .020$

This determination gives a very high value to the atomic weight of magnesium, which is unquestionably wrong. The error, probably, is due to the presence of oxychloride in the magnesium chloride taken, an

\* Ann. Chem. Pharm., 113, 33. 1860.



impurity tending to raise the apparent atomic weight of the metal. Richards' and Parker's revision of this ratio is more satisfactory.

Marignac,\* in 1883, resorted to the old method of determination, depending upon the direct ratio between  $\text{MgO}$  and  $\text{SO}_3$ . This ratio he measured both synthetically and analytically. First, magnesia from various sources was converted into sulphate. The  $\text{MgSO}_4$  from 100 parts of  $\text{MgO}$  is given in the third column:

	<i>MgO.</i>	<i>MgSO<sub>4</sub>.</i>	<i>Ratio.</i>
1.....	1.5635	4.6620	298.17
2.....	1.4087	4.2025	298.32
3.....	1.5917	4.7480	298.30
4.....	1.4705	4.3855	298.23
5.....	1.4778	4.4060	298.15
6.....	1.6267	4.8530	298.33
7.....	1.3657	4.0740	298.37
8.....	1.9575	5.8390	298.29
9.....	1.6965	5.0600	298.26
10.....	1.8680	5.5715	298.26

Mean, 298.27,  $\pm .0149$

The magnesia for experiments 1 to 5 was prepared by calcination of the nitrate, that of 6 to 8 from the sulphate, and the remaining two from the carbonate. But Richards and Rogers† have shown that magnesia derived from the nitrate always contains occluded gaseous impurity, so that the experiments depending upon its use are somewhat questionable. The results tend to give an atomic weight for magnesium which is possibly too high. Whether the other samples of magnesia are subject to similar objections I cannot say.

Marignac's second series was obtained by the calcination of the sulphate, with results as follows:

<i>MgSO<sub>4</sub>.</i>	<i>MgO.</i>	<i>Ratio.</i>
3.7795	1.2642	298.25
4.7396	1.5884	298.39
3.3830	1.1345	298.19
4.7154	1.5806	298.33
4.5662	1.5302	298.43
4.5640	1.5300	298.30
3.2733	1.0979	298.14
4.8856	1.6378	298.30
5.0092	1.6792	298.31
5.3396	1.7898	298.33
5.1775	1.7352	298.38
5.0126	1.6807	298.24
5.0398	1.6894	298.32

Mean, 298.30,  $\pm .0150$

\* Arch. Sci. Phys. et Nat. (3), 10, 206.

† Am. Chem. Journ., 15, 567. 1893.

These data may now be combined with the work of previous investigators, giving Macdonnell's one result and Jacquelain's two, each equal weight with a single experiment in Bahr's series:

Macdonnell.....	300.193, $\pm$ .1413
Jacquelain.....	297.968, $\pm$ .0999
Bahr.....	296.200, $\pm$ .0815
Svanberg and Nordenfeldt.....	296.671, $\pm$ .0720
Marignac, synthetic.....	298.27, $\pm$ .0149
Marignac, calcination.....	298.30, $\pm$ .0150
General mean.....	298.210, $\pm$ .0103

Burton and Vorce,\* who published their work on magnesium in 1890, started out with the metal itself, which had been purified by distillation in a Sprengel vacuum. This metal was dissolved in pure nitric acid, and the resulting nitrate was converted into oxide by calcination at a white heat. The oxide was carefully tested for oxides of nitrogen, which were proved to be absent, but occluded gases, the impurity pointed out by Richards and Rogers, were not suspected. This impurity must have been present, and it would tend to lower the apparent atomic weight of magnesium as calculated from the data obtained. The results were as follows, together with the percentage of Mg in MgO:

<i>Mg Taken.</i>	<i>MgO Formed.</i>	<i>Per cent. Mg.</i>
.33009	.54766	60.273
.34512	.57252	60.281
.26058	.43221	60.290
.28600	.47432	60.297
.30917	.51273	60.299
.27636	.45853	60.271
.36457	.60475	60.284
.32411	.53746	60.304
.32108	.53263	60.282
.28323	.46988	60.262
		Mean, 60.2845, $\pm$ .0027

The latest determinations of all are those of Richards and Parker,† who studied magnesium chloride with all the precautions suggested by the most recent researches. The salt itself was not only free from oxychloride, but also spectroscopically pure as regards alkaline contaminations, and all weighings were reduced to a vacuum standard. The first series of experiments gives the ratio between silver chloride and magnesium chloride, and I have reduced the data to the form  $2\text{AgCl} : \text{MgCl}_2 :: 100 : x$ . The weighings and values for  $x$  are subjoined:

\* Am. Chem. Journ., 12, 219. 1890.

† Zeitsch. Anorg. Chem., 13, 51. 1896.

<i>MgCl<sub>2</sub>.</i>	<i>AgCl.</i>	<i>Ratio.</i>
1.33550	4.01952	33.225
1.51601	4.56369	33.219
1.32413	3.98528	33.226
1.40664	4.23297	33.231
1.25487	3.77670	33.227

Mean, 33.226,  $\pm .0013$

The remaining series of experiments, three in number, relate to the ratio  $2\text{Ag} : \text{MgCl}_2$ , which was earlier investigated by Dumas. For the elaborate details of manipulation the original memoir must be consulted. I can give little more than the weights found, and their reduction to the usual form of ratio,  $\text{Ag}_2 : \text{MgCl}_2 :: 100 : x$ :

*Second Series.*

<i>MgCl<sub>2</sub>.</i>	<i>Ag.</i>	<i>Ratio.</i>
2.78284	6.30284	44.152
2.29360	5.19560	44.145
2.36579	5.35989	44.130

Mean, 44.142,  $\pm .0043$

This series gives slightly higher results than the others, and the authors, for reasons which they assign, discard it: •

*Third Series.*

<i>MgCl<sub>2</sub>.</i>	<i>Ag.</i>	<i>Ratio.</i>
1.99276	4.51554	44.131
1.78770	4.05256	44.138
2.12832	4.82174	44.140
2.51483	5.69714	44.141
2.40672	5.45294	44.136
1.95005	4.41747	44.144

Mean, 44.138,  $\pm .0013$

The fourth series, because of the experience gained in the conduct of the preceding determinations, is best of all, and the authors adopt its results in preference to the others:

*Fourth Series.*

<i>MgCl<sub>2</sub>.</i>	<i>Ag.</i>	<i>Ratio.</i>
2.03402	4.60855	44.136
1.91048	4.32841	44.138
2.09932	4.75635	44.137
1.82041	4.12447	44.137
1.92065	4.35151	44.138
1.11172	2.51876	44.138

Mean, 44.137,  $\pm .0003$

These series combine with that of Dumas as follows :

Dumas.....	44.261, $\pm .0200$
Richards and Parker, second series.....	44.142, $\pm .0043$
Richards and Parker, third series.....	44.138, $\pm .0013$
Richards and Parker, fourth series.....	44.137, $\pm .0003$
General mean.....	44.138, $\pm .0003$

Here the first two values practically vanish, and the third and fourth series of Richards and Parker appear alone.

To sum up, we now have the subjoined ratios, bearing upon the atomic weight of magnesium :

- (1.)  $\text{MgSO}_4 : \text{BaSO}_4 :: 100 : 194.003, \pm .021$
- (2.)  $\text{MgO} : \text{MgSO}_4 :: 100 : 298.210, \pm .0103$
- (3.) Per cent. of water in  $\text{MgSO}_4, 7\text{H}_2\text{O}, 51.21, \pm .020$
- (4.) Per cent. of  $\text{MgO}$  in oxalate, 27.3665,  $\pm .0023$
- (5.) Per cent. of  $\text{MgO}$  in carbonate, 47.627,  $\pm .0018$
- (6.) Per cent. of  $\text{Mg}$  in  $\text{MgO}$ , 60.2845,  $\pm .0027$
- (7.)  $2\text{Ag} : \text{MgCl}_2 :: 100 : 44.138, \pm .0003$
- (8.)  $2\text{AgCl} : \text{MgCl}_2 :: 100 : 33.226, \pm .0013$

To reduce these ratios we have—

O = 15.879, $\pm .0003$	C = 11.920, $\pm .0004$
Ag = 107.108, $\pm .0031$	Ba = 136.392, $\pm .0086$
Cl = 35.179, $\pm .0048$	AgCl = 142.287, $\pm .0037$
S = 31.828, $\pm .0015$	

For the molecular weight of  $\text{MgSO}_4$ , two values are now calculable :

From (1) .....	$\text{MgSO}_4 = 119.450, \pm .0137$
From (3) .....	" = 119.239, $\pm .0675$
General mean.....	$\text{MgSO}_4 = 119.443, \pm .0135$

Hence  $\text{Mg} = 24.099, \pm .0136$ .

For  $\text{MgO}$ , three values are found :

From (2).....	$\text{MgO} = 40.091, \pm .0023$
From (4).....	" = 40.404, $\pm .0037$
From (5).....	" = 39.721, $\pm .0021$
General mean.....	$\text{MgO} = 39.974, \pm .0014$

Hence  $\text{Mg} = 24.095, \pm .0014$ .

For  $\text{MgCl}_2$  there are two values :

From (7).....	$\text{MgCl}_2 = 94.551, \pm .0032$
From (8).....	" = 94.553, $\pm .0044$
General mean.....	$\text{MgCl}_2 = 94.552, \pm .0026$

Hence  $\text{Mg} = 24.194, \pm .0099$ .

With the aid of these intermediate values, four estimates of the atomic weight of magnesium are available, as follows :

From molecular weight of $\text{MgSO}_4$ . . . .	$\text{Mg} = 24.099, \pm .0136$
From molecular weight of $\text{MgO}$ . . . . .	" $= 24.095, \pm .0014$
From molecular weight of $\text{MgCl}_2$ . . . . .	" $= 24.194, \pm .0099$
From ratio (6) . . . . .	" $= 24.103, \pm .0020$
<hr/>	
General mean . . . . .	$\text{Mg} = 24.100, \pm .0011$

If  $\text{O} = 16$ , this becomes  $\text{Mg} = 24.283$ .

On purely chemical grounds the third of the foregoing values, that derived from magnesium chloride, seems to be the best. I should unhesitatingly adopt it, rejecting the others, were it not for the fact that it rests upon one compound of magnesium alone, and therefore is not absolutely conclusive. It agrees admirably, however, with the sulphate determinations of Marignac, and it is highly probable that it may be fully confirmed later by evidence from other sources.

Marignac's data, taken alone, give  $\text{Mg} = 24.197$ . The fourth series of Richards and Parker, by itself, gives  $\text{Mg} = 24.180$ . The approximate mean of these, 24.19, may be preferred by many chemists to the general mean derived from all the observations.

## ZINC.

The several determinations of the atomic weight of zinc are by no means closely concordant. The results obtained by Gay-Lussac\* and Berzelius † were undoubtedly too low, and may be disregarded here. We need consider only the work done by later investigators.

In 1842 Jacquelin published the results of his investigations upon this important constant. ‡ In two experiments a weighed quantity of zinc was converted into nitrate, and that by ignition in a *platinum* crucible was reduced to oxide. In two other experiments sulphuric acid took the place of nitric. As the zinc contained small quantities of lead and iron, these were estimated, and the necessary corrections applied. From the weights of metal and oxide given by Jacquelin the percentages have been calculated :

*Nitric Series.*

9.917 grm. Zn gave	12.3138 grm. ZnO.	80.536 per cent. Zn.
9.809       “	12.1800       “	80.534       “

*Sulphuric Series.*

2.398 grm. Zn gave	2.978 grm. ZnO.	80.524       “
3.197       “	3.968       “	80.570       “

Mean of all four, 80.541,  $\pm .007$

Hence  $\text{Zn} = 65.723.$

The method adopted by Axel Erdmann § is essentially the same as that of Jacquelin, but varies from the latter in certain important details. First, pure zinc oxide was prepared, ignited in a covered crucible with sugar, and then, to complete the reduction, ignited in a porcelain tube in a current of hydrogen. The pure zinc thus obtained was converted into oxide by means of treatment with nitric acid and subsequent ignition in a *porcelain* crucible. Erdmann's figures give us the following percentages of metal in the oxide :

80.247
80.257
80.263
80.274
Mean, 80.260, $\pm .0037$

Hence  $\text{Zn} = 64.562.$

\* Mémoire d'Arceuil, 2, 174.

† Gilb. Annal., 37, 460.

‡ Compt. Rend., 14, 636.

§ Poggend. Annal., 62, 611. Berz. Lehrb., 3, 1219.

Upon comparing Erdmann's results with those of Jacquelin two points are worth noticing: First, Erdmann worked with purer material than Jacquelin, although the latter applied corrections for the impurities which he knew were present; secondly, Erdmann calcined his zinc nitrate in a porcelain crucible, while Jacquelin used platinum. In the latter case it has been shown that portions of zinc may become reduced and alloy themselves with the platinum of the crucible; hence a lower weight of oxide from a given quantity of zinc, a higher percentage of metal, and an increased atomic weight. This source of constant error has undoubtedly affected Jacquelin's experiments, and vitiated his results. In Erdmann's work no such errors seem to be present.

Favre\* employed two methods of investigation. First, zinc was dissolved in sulphuric acid, the hydrogen evolved was burned, and the weight of water thus formed was determined. To his weighings I append the ratio between metallic zinc and 100 parts of water:

25.389	gram. Zn gave	6.928	gram. H <sub>2</sub> O.	366.469
30.369	"	8.297	"	366.024
31.776	"	8.671	"	366.463
				<hr/>
				Mean, 366.319, $\pm$ .088

Hence  $\text{Zn} = 65.494$ .

The second method adopted by Favre was to burn pure zinc oxalate, and to weigh the oxide and carbonic acid thus produced. From the ratio between these two sets of weights the atomic weight of zinc is easily deducible. From Favre's weighings, if  $\text{CO}_2 = 100$ ,  $\text{ZnO}$  will be as given in the third column below:

7.796	gram. ZnO =	8.365	gram. CO <sub>2</sub> .	93.198
7.342	"	7.883	"	93.137
5.2065	"	5.588	"	93.173
				<hr/>
				Mean, 93.169, $\pm$ .012

Hence  $\text{Zn} = 65.521$ .

Both of these determinations are open to objections. In the water series it was essential that the hydrogen should first be thoroughly dried before combustion, and then that every trace of water formed should be collected. A trivial loss of hydrogen or of water would tend to increase the apparent atomic weight of zinc.

In the combustion of the zinc oxalate equally great difficulties are encountered. Here a variety of errors are possible, such as are due, for example, to impurity of material, to imperfect drying of the carbon dioxide, and to incomplete collection of the latter. Indeed a fourth combustion is omitted from the series as given, having been rejected by Favre himself. In this case the oxide formed was contaminated by traces of sulphide.

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\*Ann. Chim. Phys. (3), 10, 163. 1844.

Baubigny,\* in 1883, resorted to the well-known sulphate method. Zinc sulphate, elaborately purified, was dried at  $440^{\circ}$  to constant weight, and then calcined at a temperature equal to the fusing point of gold. These data were obtained :

$ZnSO_4$ .	$ZnO$ .	Per cent. $ZnO$ .
6.699	3.377	50.410
8.776	4.4245	50.416
		<u>Mean, 50.413, <math>\pm</math> .0020</u>

Hence  $Zn = 64.909$ .

In Marignac's determinations of the atomic weight of zinc, published also in 1883,† there is a peculiar complication. After testing and criticising some other methods, he finally decided to study the double salt  $K_2ZnCl_4$ , which, however, is difficult to obtain in absolutely definite condition. Although the compound was purified by repeated crystallizations, it was found to deliquesce readily, and thereby to undergo partial dissociation, losing chloride of zinc, and leaving the porous layer on the crystalline surfaces richer in potassium. In order to evade this difficulty, Marignac placed a large quantity of the salt in a funnel, and collected the liquid product of deliquescence as it ran down. In this product he determined chlorine by volumetric titration with a standard solution of silver, and also estimated zinc by precipitation with sodium carbonate, and weighing as oxide. From the data thus obtained equations were formed, giving for each analysis an atomic weight of zinc which is independent of the proportion between  $ZnCl_2$  and  $KCl$  in the substance analyzed. The data unfortunately are too bulky for reproduction here and the calculations are complex ; but the results found for zinc, when  $Ag = 107.93$ ,  $Cl = 35.457$ , and  $K = 39.137$ , are as follows :

1. One titration. ....	$Zn = 65.22$
2. Two titrations .....	65.37
3. Two titrations .....	65.31
4. Two titrations .....	65.28
5. One titration. ....	65.26

Each of these values represents a distinct sample of the deliquesced material, and the number of chlorine determinations is indicated.

A second set of determinations was made by the same analytical method directly upon the recrystallized and carefully dried  $K_2ZnCl_4$ . The values for  $Zn$  are as follows :

6. Two titrations .....	$Zn = 65.28$
7. Two titrations .....	65.39
8. One titration. ....	65.32

\* Compt. Rend., 97, 906. 1883.

† Arch. Sci. Phys. et Nat. (3), 10, 194.



In order to adapt these data to the uniform scheme of calculation employed in this work, taking into account their probable error and the probable errors of the antecedent values for K, Cl, and Ag, it seems to be best to calculate them back with the atomic weights used by Marignac into the form of the ratio  $\text{Ag}_4 : \text{K}_2 \text{ZnCl}_4 :: 100 : x$ . Doing this, and taking each value as many times as there are titrations represented in it—that is, giving the results of a double determination twice the weight of a single one—we have the following series of data for the ratio in question :

From 1. . . . .	66.090
From 2. . . . .	{ 66.124
	{ 66.124
From 3. . . . .	{ 66.110
	{ 66.110
From 4. . . . .	{ 66.104
	{ 66.104
From 5. . . . .	66.099
From 6. . . . .	{ 66.104
	{ 66.104
From 7. . . . .	{ 66.129
	{ 66.129
From 8. . . . .	66.113
Mean, 66.111, $\pm .0023$	

Hence, from Marignac's work,  $\text{Ag}_4 : \text{K}_2 \text{ZnCl}_4 :: 100 : 66.111, \pm .0023$ , a ratio which can be discussed along with others at the close of this chapter.

During the years between 1883 and 1889, a number of determinations were made of the direct ratio between zinc and hydrogen—that is, weighed quantities of zinc were dissolved in acid, the hydrogen evolved was measured, and from its volume, with Regnault's data, the weight of H was computed. First in order are Van der Plaats' determinations,\* whose results, as given by himself, are subjoined. The weights are reduced to a vacuum. Sulphuric acid was the solvent.

<i>Zn, grms.</i>	<i>H, litres.</i>	<i>Zn =</i>
6.6725	1.1424	65.21
9.1271	1.5643	65.14
13.8758	2.3767	65.18
Mean, 65.177, $\pm .0137$		

With the new value for the weight of hydrogen, .089872 gramme per litre, this becomes  $\text{Zn} = 64.980, \pm .0137$ .

Reynolds and Ramsay made 29 determinations of this ratio.† rejecting, however, all but 5. The weighings were reduced to vacuum, and in each experiment the volume of hydrogen was fixed by the mean of seven or eight readings. The values for Zn are as follows :

\* Compt. Rend., 100, 52. 1885.

† Journ. Chem. Soc., 51, 854. 1887.

65.5060  
 65.4766  
 65.4450  
 65.5522  
 65.4141

Mean, 65.4787,  $\pm .0161$

These values were computed with Regnault's data for the weight of H. Corrected by the new value the mean becomes  $\text{Zn} = 65.280, \pm .0161$ .

A few determinations by Mallet were made incidentally to his work on the atomic weight of gold, and appear in the same paper.\* According to these experiments, one gramme of zinc gives—

341.85 cc. H., and  $\text{Zn} = 65.158$   
 341.91 “ “ 65.146  
 341.93 “ “ 65.143  
 342.04 “ “ 65.122

Mean, 65.142,  $\pm .0039$

In this case the Crafts-Regnault weight of H was taken, one litre = .08979 gramme. Corrected, the mean gives  $\text{Zn} = 65.082, \pm .0039$ .

Two other series of determinations of questionable value remain to be noticed before leaving the consideration of the direct H : Zn ratio. They represent really the practice work of students, and are interesting as an illustration of the closeness with which such work can be done. The first series was made in the laboratory of the Johns Hopkins University, under the direction of Morse and Keiser,† and contains 51 determinations, as follows :

<i>Zn</i> =		
64.68	65.74	65.40
65.26	64.72	64.80
65.32	65.26	65.20
65.20	64.74	64.40
65.60	64.72	65.00
64.60	65.10	64.40
65.00	64.76	65.24
65.68	64.90	64.60
65.38	64.92	64.80
65.06	64.64	65.14
64.84	65.24	64.84
64.88	64.72	64.82
65.00	65.20	64.80
65.08	65.12	64.40
65.06	66.40	64.60
64.74	64.60	64.80
65.12	65.60	64.74

Mean of all,  $\text{Zn} = 64.997, \pm .0328$

\* Amer. Chem. Journ., 12, 205. 1890.

† Amer. Chem. Journ., 6, 347. 1884.

Corrected for the difference between Regnault's value for H and the new value, this becomes  $\text{Zn} = 64.800, \pm .0328$ .

The second student series was published by Torrey,\* who gives 15 determinations, as follows:

$\text{Zn} =$	
65.36	64.96
65.30	64.70
64.92	65.00
64.72	64.78
65.04	64.44
64.80	65.24
65.20	64.92
64.90	
Mean, 64.952, $\pm .0436$	

Corrected as in the other series, this gives  $\text{Zn} = 64.755, \pm .0436$ .

The five corrected means for the ratio  $\text{H} : \text{Zn}$  may now be combined, thus:

Van der Plaats .....	64.980, $\pm .0137$
Reynolds and Ramsay.....	65.280, $\pm .0161$
Mallet.....	65.082, $\pm .0039$
Morse and Keiser.....	64.800, $\pm .0328$
Torrey.....	64.755, $\pm .0436$
General mean.....	65.079, $\pm .0036$

Morse and Burton,† in their determinations of the atomic weight of zinc, returned essentially to the old method adopted by Erdmann and by Jacquelin. Their zinc was obtained spectroscopically pure by distillation in a vacuum, and was oxidized by nitric acid which left absolutely no residue upon evaporation. The conversion to oxide was effected in a porcelain crucible, which was enclosed in a larger one, and the ignition of the nitrate was carried out in a muffle. In weighing, the crucible was tared by one of nearly equal weight. Results as follows:

<i>Wt. Zn.</i>	<i>Wt. ZnO.</i>	<i>Per cent. Zn in ZnO.</i>
1.11616	1.38972	80.320
1.03423	1.28782	80.308
1.11628	1.38987	80.315
1.05760	1.31681	80.316
1.04801	1.30492	80.313
1.02957	1.28193	80.318
1.09181	1.35944	80.315
1.16413	1.44955	80.305
1.07814	1.34248	80.305
1.12754	1.40400	80.306
.91112	1.13446	80.310

\* Amer. Chem. Journ., 10, 74. 1888.

† Amer. Chem. Journ., 10, 311. 1888.

1.10011	1.36981	80.311
1.17038	1.45726	80.313
1.03148	1.28436	80.310
1.05505	1.31365	80.308

Mean, 80.3115,  $\pm$  .00084.

Combining this mean with the means found by the earlier investigators, we have—

Jacquelain.....	80.541, $\pm$ .0070
Erdmann.....	80.260, $\pm$ .0037
Morse and Burton.....	80.3115, $\pm$ .00084
General mean.....	80.317, $\pm$ .0008

Morse and Burton verified by experiment the stability of oxide of zinc at the temperatures of ignition, and found that it did not dissociate. They also proved the absence of oxides of nitrogen from the zinc oxide. The investigations of Richards and Rogers,\* however, have shown that zinc oxide prepared by ignition of the nitrate always carries gaseous occlusions, so that the atomic weight of zinc computed from the data of Morse and Burton is probably too low. But for that objection, their work would leave little to be desired on the score of accuracy.

The determinations made by Gladstone and Hibbard† represent still another process for measuring the atomic weight of zinc. Zinc was dissolved in a voltameter, and the same current was used to precipitate metallic silver or copper in equivalent amount. The weight of zinc dissolved, compared with the weight of the other metal thrown down, gives the atomic weight sought for. Two voltameters were used in the experiments, giving duplicate estimates for zinc with reference to each weighing of silver or copper. The silver series is as follows, with the ratio  $\text{Ag}_2 : \text{Zn} :: 100 : x$  in the third column:

<i>Zn.</i>	<i>Ag.</i>	<i>Ratio.</i>
.7767	2.5589	30.353
.7758	2.5589	30.318
.5927	1.9551	30.316
.5924	1.9551	30.300
.2277	.7517	30.291
.2281	.7517	30.345
.7452	2.4588	30.307
.7475	2.4588	30.401
.8770	2.9000	30.241
.8784	2.9000	30.290
.9341	3.0809	30.319
.9347	3.0809	30.339

Mean, 30.318,  $\pm$  .0077

\* Proc. Amer. Acad., 1893. 200.

† Journ. Chem. Soc., 55, 443. 1889.

To the copper series I add the ratio  $\text{Cu} : \text{Zn} : : 100 : x$ .

<i>Zn.</i>	<i>Cu.</i>	<i>Ratio.</i>
.7767	.7526	103.13
.7758	.7526	103.08
.5927	.5737	103.31
.5924	.5737	103.26
.2277	.2209	103.08
.2281	.2209	103.26
.8770	.8510	103.05
.8784	.8510	103.22
.9341	.9038	103.36
.9347	.9038	103.42

Mean, 103.22,  $\pm .0261$

Richards and Rogers,\* in their investigation of the atomic weight of zinc, studied the anhydrous bromide. This was prepared by solution of zinc oxide in hydrobromic acid, evaporation to dryness, and subsequent distillation in an atmosphere of carbon dioxide. In some experiments, however, the bromide was heated in an atmosphere of nitrogen, mingled with gaseous hydrobromic acid. All water can thus be removed, without formation of oxybromides.

The zinc bromide so obtained was dissolved in water, and precipitated with a solution containing a known amount of silver in the form of nitrate. The silver bromide was weighed on a Gooch crucible, and the ratio  $2\text{AgBr} : \text{ZnBr}_2$  thus found. An excess of silver was always used, and in one series of experiments it was estimated by precipitation with hydrobromic acid. Deducting the excess thus found from the original quantity of silver, the amount of the latter proportional to the zinc bromide was found; hence the ratio  $\text{Ag}_2 : \text{ZnBr}_2$ . The results, with vacuum weights, are as follows:

*Series A.*

<i>ZnBr<sub>2</sub>.</i>	<i>AgBr.</i>	<i>Ratio.</i>
1.69616	2.82805	59.976
1.98198	3.30450	59.978
1.70920	2.84949	59.984
2.35079	3.91941	59.978
2.66078	4.43751	59.961

Mean, 59.975,  $\pm .0034$

*Series B.*

<i>ZnBr<sub>2</sub>.</i>	<i>Ag.</i>	<i>AgBr.</i>	<i>Ag Ratio.</i>	<i>AgBr Ratio.</i>
2.33882	2.24063	3.90067	104.382	59.959
1.97142	1.88837	3.28742	104.398	59.969
2.14985	2.05971	3.58539	104.376	59.961
2.00966	1.92476	3.35074	104.411	59.977

Mean, 104.392,  $\pm .0054$       Mean, 59.967,  $\pm .0027$

At the end of the same paper, Richards alone gives two more series of determinations made upon zinc bromide prepared by the action of pure bromine upon pure electrolytic zinc. The bromide so obtained was further refined by sublimation or distillation, and dried by heating in a stream of carbon dioxide and gaseous hydrobromic acid. Thus was ensured the absence of basic salts and of water. The weights and results found in the two series were as follows :

*Series C.*

<i>ZnBr<sub>2</sub>.</i>	<i>Ag.</i>	<i>Ratio.</i>
6.23833	5.9766	104.379
5.26449	5.0436	104.380
9.36283	8.9702	104.377
		<hr/>
		Mean, 104.379, $\pm .0007$

*Series D.*

<i>ZnBr<sub>2</sub>.</i>	<i>AgBr.</i>	<i>Ratio.</i>
2.65847	4.43358	59.962
2.30939	3.85149	59.961
5.26449	8.77992	59.961
		<hr/>
		Mean, 59.961, $\pm .0004$

In some details of manipulation these series differ from those given by Richards and Rogers jointly, but their minutiae are not essential to the present discussion.

Combining these several series, we have—

*For  $Ag_2 : ZnBr_2 :: 100 : x$ .*

Series B.....	104.392, $\pm .0054$
Series C.....	104.379, $\pm .0007$
<hr/>	
General mean.....	104.380, $\pm .0007$

*For  $2AgBr : ZnBr_2 :: 100 : x$ .*

Series A.....	59.975, $\pm .0034$
Series B.....	59.967, $\pm .0027$
Series D.....	59.961, $\pm .0004$
<hr/>	
General mean.....	59.962, $\pm .0004$

From the Ag ratio.....	$ZnBr_2 = 223.599, \pm .0066$
From the AgBr ratio.....	" = 223.601, $\pm .0066$
<hr/>	
General mean.....	$ZnBr_2 = 223.600, \pm .0047$
	And Zn = 64.912, $\pm .0133$

For computing the atomic weight of zinc we now have these ratios:

- (1.) Per cent. Zn in ZnO, 80.317,  $\pm .0008$
- (2.) Per cent. ZnO in ZnSO<sub>4</sub>, 50.413,  $\pm .0020$
- (3.) H<sub>2</sub>O : Zn :: 100 : 366.319,  $\pm .088$
- (4.) 2CO<sub>2</sub> : Zn :: 100 : 93.169,  $\pm .012$
- (5.) H : Zn :: 1 : 65.079,  $\pm .0036$
- (6.) Ag<sub>4</sub> : K<sub>2</sub>ZnCl<sub>4</sub> :: 100 : 66.111,  $\pm .0023$
- (7.) Ag<sub>2</sub> : Zn :: 100 : 30.318,  $\pm .0077$
- (8.) Cu : Zn :: 100 : 103.22,  $\pm .0261$
- (9.) Ag<sub>2</sub> : ZnBr<sub>2</sub> :: 100 : 104.38,  $\pm .0007$
- (10.) 2AgBr : ZnBr<sub>2</sub> :: 100 : 59.962,  $\pm .0004$

The antecedent atomic weights, with H = 1, are—

O = 15.879, $\pm .0003$	C = 11.920, $\pm .0004$
Cl = 35.179, $\pm .0048$	S = 31.828, $\pm .0015$
Br = 79.344, $\pm .0062$	Cu = 63.119, $\pm .0015$
Ag = 107.108, $\pm .0031$	AgBr = 186.452, $\pm .0054$
K = 38.817, $\pm .0051$	

With these data, combining ratios 9 and 10 into one (see preceding paragraphs), we have nine independent values for the atomic weight of zinc, as follows:

From (1) . . . . .	Zn = 64.795, $\pm .0030$
From (2) . . . . .	" = 64.909, $\pm .0073$
From (3) . . . . .	" = 65.494, $\pm .0019$
From (4) . . . . .	" = 65.521, $\pm .0115$
From (5) . . . . .	" = 65.079, $\pm .0036$
From (6) . . . . .	" = 64.891, $\pm .0253$
From (7) . . . . .	" = 64.947, $\pm .0166$
From (8) . . . . .	" = 65.151, $\pm .0166$
From (9) and (10) . . . . .	" = 64.912, $\pm .0133$
<hr/>	
General mean of all . . . . .	Zn = 65.152, $\pm .0014$
With O = 16. . . . .	Zn = 65.650

Of these values, Nos. 3 and 4, representing Favre's work, are unquestionably far wrong. Rejecting them, the general mean of the remaining seven values becomes—

$$\text{Zn} = 64.912, \pm .0021.$$

If O = 16, this gives Zn = 65.407. These figures are identical, except as regards the lower probable error, with the result deduced from Richards and Rogers' determinations alone, and they may be taken as satisfactory.

## CADMIUM.

The earliest determination of the atomic weight of this metal was by Stromeyer, who found that 100 parts of cadmium united with 14.352 of oxygen.\* With our value for the atomic weight of oxygen, these figures make  $\text{Cd} = 110.64$ . This result has now only a historical interest.

The more modern estimates of the atomic weight of cadmium begin with the work of v. Hauer.† He heated pure anhydrous cadmium sulphate in a stream of dry hydrogen sulphide, and weighed the cadmium sulphide thus obtained. His results were as follows, with the percentage of  $\text{CdS}$  in  $\text{CdSO}_4$  therefrom deduced :

7.7650	gram.	$\text{CdSO}_4$	gave	5.3741	gram.	$\text{CdS}$ .	69.209	per cent.
6.6086	"	"		4.5746	"	"	69.222	"
7.3821	"	"		5.1117	"	"	69.245	"
6.8377	"	"		4.7336	"	"	69.228	"
8.1956	"	"		5.6736	"	"	69.227	"
7.6039	"	"		5.2634	"	"	69.220	"
7.1415	"	"		4.9431	"	"	69.217	"
5.8245	"	"		4.0335	"	"	69.251	"
6.8462	"	"		4.7415	"	"	69.257	"

Mean, 69.231,  $\pm .0042$

Lessen‡ worked upon pure cadmium oxalate, handling, however, only small quantities of material. This salt, upon ignition, leaves the following percentages of oxide:

.5128	gram.	oxalate	gave	.3281	gram.	$\text{CdO}$ .	63.982	per cent.
.6552	"	"		.4193	"	"	63.996	"
.4017	"	"		.2573	"	"	64.053	"

Mean, 64.010,  $\pm .014$

Dumas|| dissolved pure cadmium in hydrochloric acid, evaporated the solution to dryness, and fused the residue in hydrochloric acid gas. The cadmium chloride thus obtained was dissolved in water and titrated with a solution of silver after the usual manner. From Dumas' weighings I calculate the ratio between  $\text{CdCl}_2$  and 100 parts of silver:

2.369	gram.	$\text{CdCl}_2$	=	2.791	gram.	$\text{Ag}$ .	84.880
4.540	"	"		5.348	"	"	84.892
6.177	"	"		7.260	"	"	85.083
2.404	"	"		2.841	"	"	84.618
3.5325	"	"		4.166	"	"	84.794
4.042	"	"		4.767	"	"	84.791

Mean, 84.843,  $\pm .026$

\* See Berz. Lehrbuch, 5th Aufl., 3, 1219.

† Journ. für Prakt. Chem., 72, 350. 1857.

‡ Journ. für Prakt. Chem., 79, 281. 1860.

|| Ann. Chem. Pharm., 113, 27. 1860.



Next in order comes Huntington's\* work, carried out in the laboratory of J. P. Cooke. Bromide of cadmium was prepared by dissolving the carbonate in hydrobromic acid, and the product, dried at  $200^{\circ}$ , was purified by sublimation in a porcelain tube. Upon the compound thus obtained two series of experiments were made.

In one series the bromide was dissolved in water, and a quantity of silver not quite sufficient for complete precipitation of the bromine was then added in nitric acid solution. After the precipitate had settled, the supernatant liquid was titrated with a standard solution of silver containing one gramme to the litre. The precipitate was washed by decantation, collected by reverse filtration, and weighed. To the weighings I append the ratio between  $\text{CdBr}_2$  and 100 parts of silver bromide :

1.5592	gram.	$\text{CdBr}_2$	gave	2.1529	gram.	$\text{AgBr}$ .	Ratio, 72.423
* 3.7456	"			5.1724	"		" 72.415
2.4267	"			3.3511	"		" 72.415
* 3.6645	"			5.0590	"		" 72.435
* 3.7679	"			5.2016	"		" 72.437
2.7938	"			3.8583	"		" 72.410
* 1.9225	"			2.6552	"		" 72.405
3.4473	"			4.7593	"		" 72.433
							Mean, 72.4216, $\pm .0028$

The second series was like the first, except that the weight of silver needed to effect precipitation was noted, instead of the weight of silver bromide formed. In the experiments marked with an asterisk, both the amount of silver required and the amount of silver bromide thrown down were determined in one set of weighings. The third column gives the  $\text{CdBr}_2$  proportional to 100 parts of silver :

* 3.7456	gram.	$\text{CdBr}_2$	=	2.9715	gram.	$\text{Ag}$ .	126.051
5.0270	"			3.9874	"		126.072
* 3.6645	"			2.9073	"		126.045
* 3.7679	"			2.9888	"		126.067
* 1.9225	"			1.5248	"		126.082
2.9101	"			2.3079	"		126.093
3.6510	"			2.8951	"		126.110
3.9782	"			3.1551	"		126.088
							Mean, 126.076, $\pm .0052$

According to Huntington's own calculations, these experiments fix the ratio between silver, bromine, and cadmium as  $\text{Ag} : \text{Br} : \text{Cd} :: 108 : 80 : 112.31$ .

In 1890, Partridge† published determinations of the atomic weight of cadmium, made by three methods, the weighings being reduced to

\* Proc. Amer. Acad., 1881.

† Amer. Journ. Sci. (3), 40, 377. 1890.

vacuum standards throughout. First, Lenssen's method was followed, viz., the ignition of the oxalate, with the subjoined results:

$CdC_2O_4$ .	$CdO$ .	<i>Per cent. CdO.</i>
1.09898	.70299	63.966
1.21548	.77746	63.962
1.10711	.70807	63.957
1.17948	.75440	63.959
1.16066	.74327	63.959
1.17995	.75471	63.964
1.34227	.85864	63.968
1.43154	.91573	63.970
1.53510	.98197	63.968
1.41311	.90397	63.971

Mean, 63.964,  $\pm .0010$

Secondly, v. Hauer's experiments were repeated, cadmium sulphate being reduced to sulphide by heating in a stream of  $H_2S$ . The following data were obtained:

$CdSO_4$ .	$CdS$ .	<i>Per cent. CdS.</i>
1.60514	1.11076	69.204
1.55831	1.07834	69.197
1.67190	1.15669	69.185
1.66976	1.15554	69.200
1.40821	.97450	69.202
1.56290	1.08156	69.205
1.63278	1.12985	69.194
1.58270	1.09524	69.198
1.53873	1.06481	69.201
1.70462	1.17962	69.201

Mean, 69.199,  $\pm .0012$

v. Hauer found, 69.231,  $\pm .0042$

General mean, 69.202,  $\pm .0012$

In the third set of determinations cadmium oxalate was transformed to sulphide by heating in  $H_2S$ , giving the ratio  $CdC_2O_4 : CdS :: 100 : x$ .

$CdC_2O_4$ .	$CdS$ .	<i>Per cent CdS.</i>
1.57092	1.13065	71.972
1.73654	1.24979	71.973
2.19276	1.57825	71.974
1.24337	.89492	71.974
1.18743	.85463	71.975
1.54038	1.10858	71.968
1.38905	.99974	71.976
2.03562	1.46517	71.979
2.03781	1.46658	71.970
1.91840	1.38075	71.971

Mean, 71.973,  $\pm .0007$

This work of Partridge was presently discussed by Clarke,\* with reference to the concordance of the data, and it was shown that the three ratios determined could be discussed algebraically, giving values for the atomic weights of Cd, S, and C, when O = 16. These values are—

$$\begin{aligned}\text{Cd} &= 111.7850 \\ \text{C} &= 11.9958 \\ \text{S} &= 32.0002,\end{aligned}$$

and are independent of all antecedent values except that assumed for the standard, oxygen.

Morse and Jones,† starting out from cadmium purified by fractional distillation in vacuo, adopted two methods for their determinations. First, they effected the synthesis of the oxide from known weights of metal by dissolving the latter in nitric acid, evaporating to dryness, and subsequent ignition of the product. The oxide thus obtained was found to be completely free from oxides of nitrogen. The weighings, which are given below, were made in tared crucibles. The third column gives the percentage of Cd in CdO.

<i>Cd Taken.</i>	<i>CdO Found.</i>	<i>Per cent. Cd.</i>
1.77891	2.03288	87.507
1.82492	2.08544	87.508
1.74688	1.99626	87.507
1.57000	1.79418	87.505
1.98481	2.26820	87.506
2.27297	2.59751	87.504
1.75695	2.00775	87.508
1.70028	1.94305	87.505
1.92237	2.19679	87.508
1.92081	2.19502	87.508

Mean, 87.5066,  $\pm .00032$

The second method employed by Morse and Jones was that of Lenssen with cadmium oxalate. This salt they find to be somewhat hygroscopic, a property against which the operator must be on his guard. The data found are as follows:

<i>CdC<sub>2</sub>O<sub>4</sub>.</i>	<i>CdO.</i>	<i>Per cent. CdO.</i>
1.53937	.98526	64.004
1.77483	1.13582	63.996
1.70211	1.08949	64.008
1.70238	1.08967	64.004
1.74447	1.11651	64.003

Mean, 64.003,  $\pm .0042$

Lorimer and Smith, like Morse and Jones, determined the atomic weight of cadmium by means of the oxide, but by analysis instead of

\* Am. Chem. Journ., 13, 34. 1891.

† Am. Chem. Journ., 14, 261. 1892.

synthesis. Weighed quantities of oxide were dissolved in potassium cyanide solution, from which metallic cadmium was thrown down electrolytically. The weights are reduced to vacuum standards.

<i>CdO Taken.</i>	<i>Cd Found.</i>	<i>Per cent. Cd.</i>
.34767	.39418	87.491
.41538	.36352	87.515
1.04698	.91618	87.507
1.04066	.91500	87.493
1.26447	1.10649	87.506
.78493	.68675	87.492
.86707	.75884	87.518
.67175	.58785	87.510
1.44362	1.26329	87.508

Mean, 87.5044,  $\pm .0023$

Mr. Bucher's dissertation\* upon the atomic weight of cadmium does not claim to give any final measurements, but rather to discuss the various methods by which that constant has been determined. Nevertheless, it gives many data which seem to have positive value, and which are certainly fit for discussion along with those which have preceded this paragraph. Bucher begins with cadmium purified by distillation nine times in vacuo, and from this his various compounds were prepared. His first series of determinations was made by reducing cadmium oxalate to oxide, the oxalate having been dried fifty hours at 150°. The reduction was effected by heating in jacketed porcelain crucibles, with various precautions, and the results obtained, reduced to vacuum standards, are as follows :

<i>Oxalate.</i>	<i>Oxide.</i>	<i>Per cent. Oxide.</i>
1.97674	1.26414	63.951
1.94912	1.24682	63.968
1.96786	1.25886	63.971
1.87099	1.19675	63.958
1.37550	.87994	63.972
1.33313	.85308	63.991
1.94450	1.24452	64.002
2.01846	1.29210	64.014

Mean, 63.978,  $\pm .0052$

Combining this with the means found by previous experimenters, we have for the percentage of oxide in oxalate—

Lenssen .....	64.010, $\pm .0140$
Partridge .....	63.962, $\pm .0010$
Morse and Jones.....	64.003, $\pm .0042$
Bucher.....	63.978, $\pm .0052$
General mean.....	63.966, $\pm .0010$

\* "An examination of some methods employed in determining the atomic weight of cadmium." Johns Hopkins University doctoral dissertation. By John E. Bucher. Baltimore, 1895.

Bucher's next series of determinations was by Partridge's method—the conversion of cadmium oxalate into cadmium sulphide by heating in a stream of sulphuretted hydrogen. The sulphide was finally cooled in a current of dry nitrogen. The vacuum weights and ratios are subjoined :

<i>Oxalate.</i>	<i>Sulphide.</i>	<i>Percentage.</i>
2.56319	1.84716	72.065
2.18364	1.57341	72.055
2.11643	1.52462	72.037
3.13105	2.25582	72.047
		Mean, 72.051, $\pm .0127$
		Partridge found, 71.973, $\pm .0007$
		General mean, 71.974, $\pm .0007$

Here Bucher's mean practically vanishes.

The third method employed by Bucher was that of weighing cadmium chloride, dissolving in water, precipitating with silver nitrate, and weighing the silver chloride found. The cadmium chloride was prepared, partly by solution of cadmium in hydrochloric acid, evaporation to dryness, and sublimation in vacuo; and partly by the direct union of the metal with chlorine. The silver chloride was weighed in a Gooch crucible, with platinum sponge in place of the asbestos. To the vacuum weights I append the ratio  $2\text{AgCl} : \text{CdCl}_2 :: 100 : x$ .

<i>CdCl<sub>2</sub>.</i>	<i>AgCl.</i>	<i>Ratio.</i>
3.09183	4.83856	63.900
2.26100	3.53854	63.896
1.35729	2.12431	63.893
2.05582	3.21727	63.899
1.89774	2.97041	63.886
3.50367	5.48473	63.880
2.70292	4.23087	63.886
4.24276	6.63598	63.936
3.40200	5.32314	63.910
4.60659	7.20386	63.946
2.40832	3.76715	63.930
2.19144	3.42724	63.942
2.84628	4.45477	63.893
2.56748	4.01651	63.923
2.31003	3.61370	63.924
1.25008	1.95652	63.893
1.96015	3.06541	63.944
2.29787	3.59391	63.938
1.94227	3.03811	63.915
1.10976	1.73547	63.946
1.63080	2.55016	63.949

Mean, 63.916,  $\pm .0032$

Bucher gives a rather full discussion of the presumable errors in this method, which, however, he regards as somewhat compensatory. The

series is followed by a similar one with cadmium bromide, the latter having been sublimed in vacuo. Results as follows:

<i>CdBr<sub>2</sub></i>	<i>AgBr</i>	<i>Ratio</i>
4.39941	6.07204	72.454
3.18030	4.38831	72.472
3.60336	4.97150	72.480
4.04240	5.58062	72.453
3.60505	4.97519	72.461
		Mean, 72.464, $\pm .0035$
		Huntington found, 72.4216, $\pm .0028$
		General mean, 72.438, $\pm .0022$

In order to fix a minimum value for the atomic weight of cadmium, Bucher effected the synthesis of the sulphate from the metal. 1.15781 grammes of cadmium gave 2.14776 of sulphate.

Hence Cd = 111.511.

The sulphate produced was dried at 400°, and afterwards examined for free sulphuric acid, giving a correction which was applied to the weighings. The corrected weight is given above. Any impurity in the sulphate would tend to lower the apparent atomic weight of cadmium, and therefore the result is believed by the author to be a minimum.

Finally, Bucher examined the oxide method followed by Morse and Jones. The syntheses of oxide were effected in double crucibles, first with both crucibles porcelain, and afterwards with the small inner crucible of platinum. Two experiments were made by the first method, three by the last. Weights and percentages (Cd in CdO) as follows:

<i>Cd</i>	<i>CdO</i>	<i>Percentage</i>
{ 1.26142	1.44144	87.511
{ .99785	1.14035	87.504
		Mean, 87.508
{ 1.11321	1.27247	87.484
{ 1.02412	1.17054	87.491
{ 2.80960	3.21152	87.487
		Mean, 87.487
		Mean of all as one series, 87.495, $\pm .0035$

The two means given above, representing work done with porcelain and with platinum crucibles, correspond to a difference of about 0.2 in the atomic weight of cadmium. Experiments were made with pure oxide of cadmium by converting it into nitrate and then back to oxide, exactly as in the foregoing syntheses. In each case the oxide obtained at the end of the operation represented an increase in weight, but the increase was greater in platinum than in porcelain. Hence the weighings of cadmium oxide in the foregoing determinations probably are subject to constant errors, and cannot be trusted to fix the atomic weight

of cadmium. Their mean, taken in one series, has really no significance; but as the computations in this work involve a study of compensation of errors, the data may be combined with their predecessors, as follows:

Morse and Jones.....	87.5066, $\pm .00032$
Lorimer and Smith.....	87.5044, $\pm .0023$
Bucher.....	87.495, $\pm .0035$
General mean.....	87.5064, $\pm .0003$

This is equivalent to the absolute rejection of Bucher's data, and is therefore not wholly fair to them. His work throws doubt upon the validity of the ratio, as determined, altogether.

The latest determinations relative to the atomic weight of cadmium are those of Hardin,\* who effected the electrolysis of the chloride and bromide, and also made a direct comparison between cadmium and silver. The aqueous solutions of the salts, mixed with potassium cyanide, were electrolyzed in platinum dishes. The cadmium which served as the starting point for the investigation was purified by distillation in hydrogen. All weights are reduced to a vacuum. The data for the chloride series are as follows, with a column added for the percentage of Cd in  $\text{CdCl}_2$ :

<i>Weight CdCl<sub>2</sub>.</i>	<i>Weight Cd.</i>	<i>Percentage Cd.</i>
.43140	.26422	61.247
.49165	.30112	61.247
.71752	.43942	61.241
.72188	.44208	61.241
.77264	.47319	61.245
.81224	.49742	61.240
.90022	.55135	61.246
1.02072	.62505	61.236
1.26322	.77365	61.244
1.52344	.93314	61.252
		Mean, 61.244, $\pm .0010$ .

The results for the bromide, similarly stated, are these:

<i>Weight CdBr<sub>2</sub>.</i>	<i>Weight Cd.</i>	<i>Percentage Cd.</i>
.57745	.23790	41.198
.76412	.31484	41.203
.91835	.37842	41.207
1.01460	.41808	41.206
1.15074	.47414	41.203
1.24751	.51392	41.196
1.25951	.51905	41.210
1.51805	.62556	41.208
1.63543	.67378	41.199
2.15342	.88722	41.200
		Mean, 41.203, $\pm .0010$ .

\* Journ. Amer. Chem. Soc., 18, 1016. 1896.

The direct comparison of cadmium and silver was effected by the simultaneous electrolysis, in the same current, of double cyanide solutions. Silver was thrown down in one platinum dish, and cadmium in another. The process was not altogether satisfactory, and gave divergent results, those which are cited below having been selected by Hardin from the mass of data obtained. I have added in a third column the cadmium proportional to 100 parts of silver :

<i>Weight Cd.</i>	<i>Weight Ag.</i>	<i>Ratio.</i>
.12624	.24335	51.876
.11032	.21262	51.886
.12720	.24515	51.887
.12616	.24331	51.852
.22058	.42520	51.877
		<hr/>
		Mean, 51.876, $\pm$ .0041

For cadmium we now have the following ratios :

- (1.) Per cent. of Cd in CdO, 87.5064,  $\pm$  .0003
- (2.) Per cent. of CdO in CdC<sub>2</sub>O<sub>4</sub>, 63.966,  $\pm$  .0010
- (3.) Per cent. of CdS from CdC<sub>2</sub>O<sub>4</sub>, 71.974,  $\pm$  .0007
- (4.) Per cent. of CdS from CdSO<sub>4</sub>, 69.202,  $\pm$  .0012
- (5.) Ag<sub>2</sub> : CdCl<sub>2</sub> : : 100 : 84.843,  $\pm$  .0260
- (6.) 2AgCl : CdCl<sub>2</sub> : : 100 : 63.916,  $\pm$  .0032
- (7.) Ag<sub>2</sub> : CdBr<sub>2</sub> : : 100 : 126.076,  $\pm$  .0052
- (8.) 2AgBr : CdBr<sub>2</sub> : : 100 : 72.438,  $\pm$  .0022
- (9.) Per cent. of Cd in CdCl<sub>2</sub>, 61.244,  $\pm$  .0010
- (10.) Per cent. of Cd in CdBr<sub>2</sub>, 41.203,  $\pm$  .0010
- (11.) 2Ag : Cd : : 100 : 51.876,  $\pm$  .0041

Bucher's single experiment upon the synthesis of the sulphate, although important and interesting, cannot carry weight enough to warrant its consideration in connection with the other ratios, and is therefore not included.

The antecedent values, for use in computation are—

O = 15.879, $\pm$ .0003	S = 31.828, $\pm$ .0015
Ag = 107.108, $\pm$ .0031	C = 11.920, $\pm$ .0004
Cl = 35.179, $\pm$ .0048	AgCl = 142.287, $\pm$ .0037
Br = 79.344, $\pm$ .0062	AgBr = 186.452, $\pm$ .0054

For the molecular weight of cadmium chloride, two values are now deducible :

From (5).....	CdCl <sub>2</sub> = 181.739, $\pm$ .0560
From (6).....	“ = 181.888, $\pm$ .0103
<hr/>	
General mean.....	CdCl <sub>2</sub> = 181.883, $\pm$ .0138

Hence Cd = 111.525,  $\pm$  .0138.



For cadmium bromide we have—

From (7).....	$\text{CdBr}_2 = 270.073, \pm .0136$
From (8).....	“ = $270.124, \pm .0113$
General mean.....	$\text{CdBr}_2 = 270.105, \pm .0087$

Hence  $\text{Cd} = 111.417, \pm .0151$ .

For cadmium there are nine independent values, as follows :

From (3).....	$\text{Cd} = 110.793, \pm .0081$
From (4).....	“ = $110.890, \pm .0069$
From (2).....	“ = $111.004, \pm .0047$
From (11).....	“ = $111.127, \pm .0095$
From (9).....	“ = $111.183, \pm .0155$
From (10).....	“ = $111.202, \pm .0093$
From (1).....	“ = $111.227, \pm .0034$
From molecular weight $\text{CdBr}_2$ .....	“ = $111.417, \pm .0151$
From molecular weight $\text{CdCl}_2$ . . . .	“ = $111.525, \pm .0138$
General mean.....	$\text{Cd} = 111.100, \pm .0022$

If  $\text{O} = 16$ ,  $\text{Cd} = 111.947$ .

This result is obviously uncertain. The data are far from being conclusive, however, and I am therefore inclined to trust the mean rather than any one of the values taken separately. It is quite possible that the highest of all the figures may be nearest the truth, as Bucher's experiments seem to indicate; but until new evidence is obtained it would hardly be wise to make any selection. The mean obtained agrees well with the data of Morse and Jones, Lorimer and Smith, and Hardin.

## MERCURY.

In dealing with the atomic weight of mercury we may reject the early determinations by Sefström\* and a large part of the work done by Turner.† The latter chemist, in addition to the data which will be cited below, gives figures to represent the percentage composition of both the chlorides of mercury; but these results are neither reliable nor in proper shape to be used.

First in order we may consider the percentage composition of mercuric oxide, as established by Turner and by Erdmann and Marchand. In both investigations the oxide was decomposed by heat, and the mercury was accurately weighed. Gold leaf served to collect the last traces of mercurial vapor.

Turner gives four estimations. Two represent oxide obtained by the ignition of the nitrate, and two are from commercial oxide. In the first two the oxide still contained traces of nitrate, but hardly in weighable proportions. A comparison of the figures from this source with the others is sufficiently conclusive on this point. The third column represents the percentage of mercury in HgO:

144.805 grains Hg = 11.54 grains O.	92.619 per cent.
125.980        "        10.08        "	92.592        "
173.561        "        13.82        "	92.625        "
114.294        "        9.101        "	92.620        "

Mean, 92.614,  $\pm .0050$

In the experiments of Erdmann and Marchand‡ every precaution was taken to ensure accuracy. Their weighings, reduced to a vacuum standard, give the subjoined percentages:

82.0079 gm. HgO gave 75.9347 gm. Hg.	92.594 per cent.
51.0320        "        47.2538        "	92.597        "
84.4996        "        78.2501        "	92.604        "
44.6283        "        41.3285        "	92.606        "
118.4066        "        109.6408        "	92.597        "

Mean, 92.5996,  $\pm .0015$

Hardin's determination of the same ratio, being different in character, will be considered later.

With a view to establishing the atomic weight of sulphur, Erdmann and Marchand also made a series of analyses of pure mercuric sulphide. These data are now best available for discussion under mercury. The

\*Sefström. Berz. Lehrb., 5th ed., 3, 1215. Work done in 1812.

† Phil. Trans., 1833, 531-535.

‡ Journ. für Prakt. Chem., 31, 395. 1844.

sulphide was mixed with pure copper and ignited, mercury distilling over and copper sulphide remaining behind. Gold leaf was used to retain traces of mercurial vapor, and the weighings were reduced to vacuum :

34.3568	gim.	HgS gave	29.6207	grm.	Hg.	86.215	per cent.	Hg.
24.8278		"	21.40295		"	86.206		"
37.2177		"	32.08416		"	86.207		"
80.7641		"	69.6372		"	86.223		"

Mean, 86.2127,  $\pm .0027$

For the percentage of mercury in mercuric chloride we have data by Turner, Millon, Svanberg, and Hardin. Turner,\* in addition to some precipitations of mercuric chloride by silver nitrate, gives two experiments in which the compound was decomposed by pure stannous chloride, and the mercury thus set free was collected and weighed. The results were as follows :

44.782	grains Hg =	15.90	grains Cl.	73.798	per cent.
73.09		"	25.97		"

Mean, 73.791,  $\pm .005$

Millon† purified mercuric chloride by solution in ether and sublimation, and then subjected it to distillation with lime. The mercury was collected as in Erdmann and Marchand's experiments. Percentages of metal as follows :

73.87  
73.81  
73.83  
73.87

Mean, 73.845,  $\pm .010$

Svanberg,‡ following the general method of Erdmann and Marchand, made three distillations of mercuric chloride with lime, and got the following results :

12.048	grm.	HgCl <sub>2</sub> gave	8.889	grm.	Hg.	73.780	per cent.
12.529		"	9.2456		"	73.794	"
12.6491		"	9.3363		"	73.810	"

Mean, 73.795,  $\pm .006$

The most recent determinations of the atomic weight of mercury are due to Hardin,§ whose methods were entirely electrolytic. First, pure mercuric oxide was dissolved in dilute, aqueous potassium cyanide, and

\* Phil. Trans., 1833, 531-535.

† Ann. Chim. Phys. (3), 18, 345. 1846.

‡ Journ. für Prakt. Chem., 45, 472. 1848.

§ Journ. Amer. Chem. Soc., 18, 1003. 1896.

electrolyzed in a platinum dish. Six determinations are published, out of a larger number, but without reduction of the weights to a vacuum. The data, with a percentage column added, are as follows:

<i>Weight HgO.</i>	<i>Weight Hg.</i>	<i>Per cent. Hg.</i>
.26223	.24281	92.594
.23830	.22065	92.593
.23200	.21482	92.595
.14148	.13100	92.593
.29799	.27592	92.594
.19631	.18177	92.593

Mean, 92.594,  $\pm .0003$ .

Various sources of error were detected in these experiments, and the series is therefore rejected by Hardin. It combines with previous series as follows:

Turner.....	92.614, $\pm .0050$
Erdmann and Marchand.....	92.5996, $\pm .0015$
Hardin, .....	92.594, $\pm .0003$
General mean,.....	92.595, $\pm .0003$

Hardin also studied mercuric chloride, bromide, and cyanide, and the direct ratio between mercury and silver, with reduction of weights to a vacuum. Electrolysis was conducted in a platinum dish, as usual. With the chloride and bromide, the solutions were mixed with dilute potassium cyanide. The data for the chloride are as follows, the percentage column being added by myself:

<i>Weight HgCl<sub>2</sub>.</i>	<i>Weight Hg.</i>	<i>Per cent. Hg.</i>
.45932	.33912	73.831
.54735	.40415	73.838
.56002	.41348	73.833
.63586	.46941	73.823
.64365	.47521	73.831
.73281	.54101	73.827
.86467	.63840	73.832
1.06776	.78825	73.823
1.07945	.79685	73.820
1.51402	1.11780	73.830

Mean, 73.829,  $\pm .0012$

Combining this with the earlier determinations, we have—

Turner .....	73.791, $\pm .0050$
Millon.....	73.845, $\pm .0100$
Svanberg.....	73.795, $\pm .0060$
Hardin.....	73.829, $\pm .0012$
General mean,.....	73.826, $\pm .0011$

For the bromide Hardin's data are—

<i>Weight HgBr<sub>2</sub>.</i>	<i>Weight Hg.</i>	<i>Per cent. Hg.</i>
.70002	.38892	55.558
.56430	.31350	55.555
.57142	.31750	55.563
.77285	.42932	55.550
.80930	.44955	55.548
.85342	.47416	55.560
1.11076	.61708	55.555
1.17270	.65145	55.551
1.26186	.70107	55.559
1.40142	.77870	55.565
		<hr/>
		Mean, 55.556, $\pm .0012$

And for the cyanide—

<i>Weight HgC<sub>2</sub>N<sub>2</sub>.</i>	<i>Weight Hg.</i>	<i>Per cent. Hg.</i>
.55776	.44252	79.337
.63290	.50215	79.341
.70652	.56053	79.337
.80241	.63663	79.340
.65706	.52130	79.338
.81678	.64805	79.342
1.07628	.85392	79.340
1.22615	.97282	79.339
1.66225	1.31880	79.338
2.11170	1.67541	79.339
		<hr/>
		Mean, 79.339, $\pm .0004$

In the last series cited no potassium cyanide was used, but the solution of mercuric cyanide, with the addition of one drop of sulphuric acid, was electrolyzed directly.

The direct ratio between silver and mercury was determined by throwing down the two metals, simultaneously, in the same electric current. Both metals were taken in double cyanide solution. With Hardin's equivalent weights I give a third column, showing the quantity of mercury corresponding to 100 parts of silver. Many experiments were rejected, and only the following seven are published by the author:

<i>Weight Hg.</i>	<i>Weight Ag.</i>	<i>Ratio.</i>
.06126	.06610	92.678
.06190	.06680	92.665
.07814	.08432	92.671
.10361	.11181	92.666
.15201	.16402	92.678
.26806	.28940	92.626
.82808	.89388	92.639
		<hr/>

Mean, 92.660,  $\pm .0051$

We now have six ratios involving the atomic weight of mercury, as follows :

- (1.) Per cent. of Hg in HgO,  $92.595, \pm .0003$
- (2.) Per cent. of Hg in HgS,  $86.2127, \pm .0027$
- (3.) Per cent. of Hg in HgCl<sub>2</sub>,  $73.826, \pm .0011$
- (4.) Per cent. of Hg in HgBr<sub>2</sub>,  $55.556, \pm .0012$
- (5.) Per cent. of Hg in HgC<sub>2</sub>N<sub>2</sub>,  $79.339, \pm .0004$
- (6.) 2Ag : Hg : : 100 : 92.660,  $\pm .0051$

The calculations involve the following values :

O = 15.879, $\pm .0003$	Br = 79.344, $\pm .0062$
Ag = 107.108, $\pm .0031$	S = 31.828, $\pm .0015$
Cl = 35.179, $\pm .0048$	C = 11.920, $\pm .0004$
	N = 13.935, $\pm .0021$

Hence the values for mercury are—

From (1).....	Hg = 198.557, $\pm .0084$
From (2).....	" = 199.027, $\pm .0406$
From (3).....	" = 198.482, $\pm .0285$
From (4) ..	" = 198.364, $\pm .0170$
From (5).....	" = 198.568, $\pm .0170$
From (6).....	" = 198.493, $\pm .0124$
<hr/>	
General mean,.....	Hg = 198.532, $\pm .0059$

If O = 16, Hg = 200.045.

But according to Hardin the value derived from the analyses of mercuric oxide is untrustworthy. Rejecting this, and also the abnormally high result from the sulphide series, the general mean of the four remaining values is—

$$\text{Hg} = 198.491, \pm .0083,$$

or, with O = 16, Hg = 200.004. These figures seem to be the best for the atomic weight of mercury.

## BORON.

In the former edition of this work the data relative to boron were few and unimportant. There was a little work on record by Berzelius and by Laurent, and this was eked out by a discussion of Deville's analyses of boron chloride and bromide. As the latter were not intended for atomic weight determinations they will be omitted from the present recalculation, which includes the later researches of Hoskyns-Abraham, Ramsay and Aston, and Rimbach.

Berzelius\* based his determination upon three concordant estimations of the percentage of water in borax. Laurent† made use of two similar estimations, and all five may be properly put in one series, thus :

47.10	} Berzelius.
47.10	
47.10	
47.15	} Laurent.
47.20	
<hr/>	
Mean, 47.13, $\pm .013$	

In 1892 the posthumous notes of the late Hoskyns-Abraham were edited and published by Ewan and Hartog.‡ This chemist especially studied the ratio between boron bromide and silver, and also redetermined the percentage of water in crystallized borax. The latter work, which was purely preliminary, although carried out with great care, gave the following results, reduced to vacuum standards :

$Na_2B_4O_7 \cdot 10H_2O$ .	$Na_2B_4O_7$ .	Per cent. $H_2O$ .
7.00667	3.69587	47.2069
12.95936	6.82560	47.3308
4.65812	2.45248	47.3504
4.47208	3.93956	47.2763
4.94504	2.60759	47.2686
		<hr/>
		Mean, 47.2866, $\pm .0171$

Two sets of determinations were made with the bromide, which was prepared from boron and bromine directly, freed from excess of the latter by standing over mercury, and finally collected, after distillation, in small, weighed, glass bulbs. It was titrated with a solution of silver after all the usual precautions. The first series of experiments was as follows, with  $BBr_3$  proportional to 100 parts of silver stated as the ratio :

\* Poggend. Annalen, 8, 1. 1826.

† Journ. für Prakt. Chem., 47, 415. 1849.

‡ Journ. Chem. Soc., 61, 650. August, 1892.

<i>BBr<sub>3</sub></i> .	<i>Ag.</i>	<i>Ratio.</i>
1.31203	1.69406	77.449
4.39944	5.67829	77.478
5.04022	6.50820	77.444
6.51597	8.38919	77.433
7.75343	10.01235	77.439

Mean, 77.449,  $\pm .0053$

This series of data is regarded by the editors as preliminary, and not entitled to much consideration. The second series, which follows, was the final one; both represent vacuum standards :

<i>BBr<sub>3</sub></i> .	<i>Ag.</i>	<i>Ratio.</i>
4.467835	5.771268	77.415
8.423151	10.880648	77.414
1.655111	2.137593	77.429
8.032352	10.374201	77.426
4.092743	5.285949	77.427
2.389993	3.086842	77.425
7.721944	9.974054	77.420

Mean, 77.422,  $\pm .0018$

First series, 77.449,  $\pm .0053$

General mean, 77.425,  $\pm .0017$

Ramsay and Aston,\* in their paper upon the atomic weight of boron, suggest that Abrahall's bromide may have contained hydrobromic acid, which would fully account for the low result obtained. They themselves adopt two distinct methods, the first one being the time-honored determination of water in crystallized borax. The latter was prepared from pure boric acid and pure sodium hydroxide. Results as follows, reduced to a vacuum :

<i>Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>.10H<sub>2</sub>O.</i>	<i>Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>.</i>	<i>Per cent. H<sub>2</sub>O.</i>
10.3581602	5.4784357	47.1099
5.3440080	2.8246677	47.1433
4.9962580	2.6378934	47.2026
5.7000256	3.0101127	47.1912
5.3142725	2.8065646	47.1882
4.9971924	2.6392016	47.1865
5.2366921	2.7674672	47.1524

Mean, 47.1677,  $\pm .0086$ .

This we may combine with the previous determinations, thus :

Berzelius with Laurent.....	47.13, $\pm .0130$
Hoskyns-Abrahall.....	47.2866, $\pm .0171$
Ramsay and Aston.....	47.1677, $\pm .0086$
General mean.....	47.1756, $\pm .0066$



The second method adopted by Ramsay and Aston was to distill anhydrous borax with hydrochloric acid and methyl alcohol, both scrupulously pure, thereby converting it into sodium chloride. The operation was conducted in a glass flask, and in the first series of determinations ordinary soft glass was used. This, however, was somewhat attacked, so that the sodium chloride contained silica; hence oxygen in the material of the flask had been replaced by chlorine, thereby increasing its weight, and lowering the apparent atomic weight of boron. In a second series flasks of hard combustion tubing were taken, and the error, though not absolutely avoided, was reduced to a very small amount. Both series are subjoined, together with the percentage of chloride formed; but the weights, given by the authors to seven decimal places, are only quoted to the nearest tenth milligramme. They are reduced to vacuum standards.

*First Series.*

$Na_2B_4O_7$ .	$NaCl$ .	<i>Per cent. NaCl.</i>
4.7684	2.7598	57.877
5.2740	3.0578	57.978
3.2344	1.8727	57.899
4.0862	2.3713	58.032
3.4970	2.0266	57.953
		Mean, 57.948, $\pm .0187$

*Second Series.*

$Na_2B_4O_7$ .	$NaCl$ .	<i>Per cent. NaCl.</i>
5.3118	3.0761	57.911
4.7806	2.7700	57.943
4.9907	2.8930	57.968
4.7231	2.7360	57.928
3.3138	1.9187	57.900
		Mean, 57.930, $\pm .0081$
		First series, 57.948, $\pm .0187$
		General mean of both, 57.933, $\pm .0074$

As a check upon the last series of results, the sodium chloride was dissolved in water, and precipitated with silver nitrate. The silver chloride was collected and weighed in a Gooch crucible, and its weight gives a new ratio with anhydrous borax. The cross ratio between the two chlorides, silver and sodium, has already been used in the discussion upon sodium. The new ratio I give in terms of  $Na_2B_4O_7$  equivalent to 100 parts of  $AgCl$ .

$Na_2B_4O_7$ .	$AgCl$ .	<i>Ratio.</i>
5.3118	7.5259	70.580
4.7806	6.7794	70.517
4.9907	7.0801	70.489
4.7231	6.6960	70.536
3.3138	4.6931	70.610
		<hr/>
		Mean, 70.546, $\pm .0146$

Rimbach\* based his determination of the atomic weight of boron upon the fact that boric acid is neutral to methyl orange, and that therefore it is possible to titrate a solution of borax directly with hydrochloric acid. His borax was prepared from carefully purified boric acid and sodium carbonate, and his hydrochloric acid was standardized by a series of precipitations and weighings as silver chloride. It contained 1.84983 per cent. of actual HCl. The borax, dissolved in water, was titrated by means of a weight-burette. I give the weights found in the first and second columns of the following table, and in the third column, calculated by myself, the HCl proportional to 100 parts of crystallized borax. Rimbach himself computes the percentage of  $Na_2O$  and thence the atomic weight of boron, but the ratio  $Na_2B_4O_7 \cdot 10H_2O : 2HCl$  is the ratio actually determined.

$Na_2B_4O_7 \cdot 10H_2O$ .	<i>HCl Solution.</i>	<i>Ratio.</i>
10.00214	103.1951	19.0853
15.32772	158.1503	19.0864
15.08870	155.7271	19.0917
10.12930	104.5448	19.0922
5.25732	54.2571	19.0908
15.04324	155.2307	19.0883
15.04761	155.2959	19.0908
10.43409	107.6602	19.0868
5.04713	52.0897	19.0915
		<hr/>
		Mean, 19.0893, $\pm .0006$

Obviously, this error should be increased by the probable errors involved in standardizing the acid, but they are too small to be worth considering.

The following ratios are now available for boron :

- (1) Percentage of water in  $Na_2B_4O_7 \cdot 10H_2O$ , 47.1756,  $\pm .0066$
- (2)  $3Ag : BBr_3 :: 100 : 77.425$ ,  $\pm .0017$
- (3)  $Na_2B_4O_7 : 2NaCl :: 100 : 57.933$ ,  $\pm .0074$
- (4)  $2AgCl : Na_2B_4O_7 :: 100 : 70.546$ ,  $\pm .0146$
- (5)  $Na_2B_4O_7 \cdot 10H_2O : 2HCl :: 100 : 19.0893$ ,  $\pm .0006$

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\* Berichte Deutsch. Chem. Gesell., 26, 164. 1893.

For reduction we have the antecedent atomic and molecular weights—

O = 15.879, $\pm .0003$	Na = 22.881, $\pm .0046$
Ag = 107.108, $\pm .0031$	NaCl = 58.060, $\pm .0017$
Cl = 35.179, $\pm .0048$	AgCl = 142.287, $\pm .0037$
Br = 79.344, $\pm .0062$	

For the molecular weight of  $\text{Na}_2\text{B}_4\text{O}_7$  we now have—

From (1).....	$\text{Na}_2\text{B}_4\text{O}_7 = 200.198, \pm .0377$
From (3).....	" = 200.439, $\pm .0263$
From (4).....	" = 200.756, $\pm .0419$
From (5).....	" = 200.260, $\pm .0518$
<hr/>	
General mean.....	$\text{Na}_2\text{B}_4\text{O}_7 = 200.421, \pm .0180$

Hence  $B = 10.876, \pm .0051$ .

From ratio (2),  $B = 10.753, \pm .0207$ . The two values combined give—

$$B = 10.863, \pm .0050.$$

Or, if  $O = 16$ ,  $B = 10.946$ .

If we consider ratios (1), (3), (4), and (5) separately, they give the following values for  $B$ :

From (1).....	$B = 10.821$
From (3).....	" = 10.881
From (4).....	" = 10.960
From (5).....	" = 10.836

Of these, the second and third involve the data from which, in a previous section of this work, the ratio  $\text{NaCl} : \text{AgCl}$  was computed. In using that ratio for measuring the molecular weights of its component molecules, discordance was noted, which again appears here. The chief uncertainty in it seems to be connected with ratio (4), which is therefore entitled to comparatively little credence, although its rejection is not necessary at this point. In ratio (2), Abrahall's determination, the high probable error of  $B$  is due to the also high probable error of  $3\text{Br}$ , and it is quite likely that the result is undervalued. The general mean,  $B = 10.863, \pm .0050$ , however, can hardly be much out of the way. It is certainly more probable than any one of the individual values.

## ALUMINUM.

The atomic weight of aluminum has been determined by Berzelius, Mather, Tissier, Dumas, Isnard, Terreil, Mallet, and Baubigny. The early calculations of Davy and of Thomson we may properly disregard.

Berzelius'\* determination rests upon a single experiment. He ignited 10 grammes of dry aluminum sulphate,  $\text{Al}_2(\text{SO}_4)_3$ , and obtained 2.9934 grammes of  $\text{Al}_2\text{O}_3$  as residue.

Hence  $\text{Al} = 27.103$ .

In 1835† Mather published a single analysis of aluminum chloride, from which he sought to fix the atomic weight of the metal. 0.646 gm. of  $\text{AlCl}_3$  gave him 2.056 of  $\text{AgCl}$  and 0.2975 of  $\text{Al}_2\text{O}_3$ . These figures give worthless values for Al, and are included here only for the sake of completeness. From the ratio between  $\text{AgCl}$  and  $\text{AlCl}_3$ ,  $\text{Al} = 28.584$ .

Tissier's‡ determination, also resting on a single experiment, appeared in 1858. Metallic aluminum, containing .135 per cent. of sodium, was dissolved in hydrochloric acid. The solution was evaporated with nitric acid to expel all chlorine, and the residue was strongly ignited until only alumina remained. 1.935 gm. of Al gave 3.645 gm. of  $\text{Al}_2\text{O}_3$ . If we correct for the trace of sodium in the aluminum, we have  $\text{Al} = 26.930$ .

Essentially the same method of determination was adopted by Isnard, § who, although not next in chronological order, may fittingly be mentioned here. He found that 9 gm. of aluminum gave 17 gm. of  $\text{Al}_2\text{O}_3$ . Hence  $\text{Al} = 26.8$ .

In 1858 Dumas,|| in connection with his celebrated revision of the atomic weights, made seven experiments with aluminum chloride. The material was prepared in quantity, sublimed over iron filings, and finally resublimed from metallic aluminum. Each sample used was collected in a small glass tube, after sublimation from aluminum in a stream of dry hydrogen, and hermetically enclosed. Having been weighed in the tube, it was dissolved in water, and the quantity of silver necessary for precipitating the chlorine was determined. Reducing to a common standard, his weighings give the quantities of  $\text{AlCl}_3$  stated in the third column, as proportional to 100 parts of silver:

1.8786 gm.	$\text{AlCl}_3 = 4.543$ gm.	Ag.	41.352
3.021	"	7.292 "	41.459—Bad.
2.399	"	5.802 "	41.348
1.922	"	4.6525 "	41.311
1.697	"	4.1015 "	41.375
4.3165	"	10.448 "	41.314
6.728	"	16.265 "	41.365

\* Poggend. Annal., 8, 177.

† Silliman's Amer. Journ., 27, 241.

‡ Compt. Rend., 46, 1105.

§ Compt. Rend., 66, 508. 1868.

|| Ann. Chim. Phys. (3), 55, 151. Ann. Chem. Pharm., 113, 26.

In the second experiment the  $\text{AlCl}_3$  contained traces of iron. Rejecting this experiment, the remaining six give a mean of 41.344,  $\pm .007$ . These data give a value for Al approximating to 27.5, and were for many years regarded as satisfactory. It now seems probable that the chloride contained traces of an oxy-compound, which would tend to raise the atomic weight.

In 1879 Terreil\* published a new determination of the atomic weight under consideration, based upon a direct comparison of the metal with hydrogen. Metallic aluminum, contained in a tube of hard glass, was heated strongly in a current of dry hydrochloric acid. Hydrogen was set free, and was collected over a strong solution of caustic potash. 0.410 grm. of aluminum thus were found equivalent to 508.2 cc., or .045671 grm. of hydrogen. Hence  $\text{Al} = 26.932$ .

About a year after Terreil's determination appeared, the lower value for aluminum was thoroughly confirmed by J. W. Mallet.† After giving a full résumé of the work done by others, exclusive of Isnard, the author describes his own experiments, which may be summarized as follows:

Four methods of determination were employed, each one simple and direct, and at the same time independent of the others. First, pure ammonia alum was calcined, and the residue of aluminum oxide was estimated. Second, aluminum bromide was titrated with a standard solution of silver. Third, metallic aluminum was attacked by caustic soda, and the hydrogen evolved was measured. Fourth, hydrogen was set free by aluminum, and weighed as water. Every weight was carefully verified, the verification being based upon the direct comparison, by J. E. Hilgard, of a kilogramme weight with the standard kilogramme at Washington. The specific gravity of each piece was determined, and also of all materials and vessels used in the weighings. During each weighing both barometer and thermometer were observed, so that every result represents a real weight in vacuo.

The ammonium alum used in the first series of experiments was specially prepared, and was absolutely free from ascertainable impurities. The salt was found, however, to lose traces of water at ordinary temperatures—a circumstance which tended towards a slight elevation of the apparent atomic weight of aluminum as calculated from the weighings. Two sets of experiments were made with the alum; one upon a sample air-dried for two hours at  $21^\circ$ – $25^\circ$ , the other upon material dried for twenty-four hours at  $19^\circ$ – $26^\circ$ . These sets, marked A and B respectively, differ slightly, B being the less trustworthy of the two, judged from a chemical standpoint. Mathematically it is the better of the two. Calcination was effected with a great variety of precautions, concerning which the original memoir must be consulted. To Mallet's weighings I append the percentages of  $\text{Al}_2\text{O}_3$  deduced from them:

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\* Bulletin de la Soc. Chimique, 31, 153.

† Phil. Trans., 1880, p. 1003.

*Series A.*

8.2144	gram. of the alum gave	.9258	gram. $\text{Al}_2\text{O}_3$ .	11.270	per cent.
14.0378	"	1.5825	"	11.273	"
5.6201	"	.6337	"	11.275	"
11.2227	"	1.2657	"	11.278	"
10.8435	"	1.2216	"	11.266	"

---

Mean, 11.2724,  $\pm$  .0014

*Series B.*

12.1023	gram. of the alum gave	1.3660	gram. $\text{Al}_2\text{O}_3$ .	11.287	per cent.
10.4544	"	1.1796	"	11.283	"
6.7962	"	.7670	"	11.286	"
8.5601	"	.9654	"	11.278	"
4.8992	"	.5528	"	11.283	"

---

Mean, 11.2834,  $\pm$  .0011

Combined, these series give a general mean of 11.2793,  $\pm$  .0008. Hence  $\text{Al} = 26.952$ .

The aluminum bromide used in the second series of experiments was prepared by the direct action of bromine upon the metal. The product was repeatedly distilled, the earlier portions of each distillate being rejected, until a constant boiling point of  $263.93$  at  $747$  mm. pressure was noted. The last distillation was effected in an atmosphere of pure nitrogen, in order to avoid the possible formation of oxide or oxy-bromide of aluminum; and the distillate was collected in three portions, which proved to be sensibly identical. The individual samples of bromide were collected in thin glass tubes, which were hermetically sealed after nearly filling. For the titration pure silver was prepared, and after fusion upon charcoal it was heated in a Sprengel vacuum in order to eliminate occluded gases. This silver was dissolved in specially purified nitric acid, the latter but very slightly in excess. The aluminum bromide, weighed in the sealed tube, was dissolved in water, precautions being taken to avoid any loss by splashing or fuming which might result from the violence of the action. To the solution thus obtained the silver solution was added, the silver being something less than a decigramme in deficiency. The remaining amount of silver needed to complete the precipitation of the bromine was added from a burette, in the form of a standard solution containing one milligramme of metal to each cubic centimetre. The final results were as follows, the figures in the third column representing the quantities of bromide proportional to 100 parts of silver. Series A is from the first portion of the last distillate of  $\text{AlBr}_3$ ; series B from the second portion, and series C from the third portion:

*Series A.*

6.0024	gram. $\text{AlBr}_3 =$	7.2793	gram. Ag.	82.458
8.6492	"	10.4897	"	82.454
3.1808	"	3.8573	"	82.462

*Series B.*

6.9617	gram.	AlBr <sub>3</sub> =	8.4429	gram.	Ag.	82.456
11.2041	"		13.5897	"		82.445
3.7621	"		4.5624	"		82.459
5.2842	"		6.4085	"		82.456
9.7338	"		11.8047	"		82.457

*Series C.*

9.3515	gram.	AlBr <sub>3</sub> =	11.3424	gram.	Ag.	82.447
4.4426	"		5.3877	"		82.458
5.2750	"		6.3975	"		82.454

Mean, 82.455,  $\pm$  .001

Hence Al = 26.916.

The experiments to determine the amount of hydrogen evolved by the action of caustic soda upon metallic aluminum were conducted with pure metal, specially prepared, and with caustic soda made from sodium. The soda solution was so strong as to scarcely lose a perceptible amount of water by the passage through it of a dry gas at ordinary temperature. As the details of the experiments are somewhat complex, the original memoir must be consulted for them. The following results were obtained, the weight of the hydrogen being calculated from the volume, reckoned at .089872 gramme per litre.

<i>Wt. Al.</i>	<i>Vol. H.</i>	<i>Wt. H.</i>	<i>At. Wt.</i>
.3697	458.8	.041234	26.898
.3769	467.9	.042051	26.889
.3620	449.1	.040362	26.907
.7579	941.5	.084614	26.872
.7314	907.9	.081595	26.891
.7541	936.4	.084156	26.882

Mean, 26.890,  $\pm$  .0034

The closing series of experiments was made with larger quantities of aluminum than were used in the foregoing set. The hydrogen, evolved by the action of the caustic alkali, was dried by passing it through two drying tubes containing pumice stone and sulphuric acid, and two others containing asbestos and phosphorus pentoxide. Thence it passed through a combustion tube containing copper oxide heated to redness. A stream of dry nitrogen was employed to sweep the last traces of hydrogen into the combustion tube, and dry air was afterwards passed through the entire apparatus to reoxidize the surface of reduced copper, and to prevent the retention of occluded hydrogen. The water formed by the oxidation of the hydrogen was collected in three drying tubes.

The results obtained were as follows. The third column gives the amount of water formed from 10 grammes of aluminum.

2.1704	gm. Al gave	2.1661	gm. $H_2O$ .	9.9802
2.9355	"	2.9292	"	9.9785
5.2632	"	5.2562	"	9.9867
				<hr/>
				Mean, 9.9818, $\pm .0017$

Hence  $Al = 26.867$ .

From the last two series of experiments an independent value for the atomic weight of oxygen may be calculated. It becomes  $O = 15.895$ . The closeness of this figure to some of the best determinations affords a good indication of the accuracy of Mallet's work.

In connection with Mallet's work it is worth noting that Torrey\* published a series of measurements of the  $H : Al$  ratio, representing determinations made under his direction by elementary students. These measurements are thirteen in number, and calculated with Regnault's old value for the weight of hydrogen, range from 26.661 to 27.360, or in mean, 27.049,  $\pm .323$ . Corrected by the latest value for the weight of  $H$ , this mean becomes 26.967. The result, of course, has only confirmatory significance.

By Baubigny† we have only two determinations, based upon the calcination of anhydrous aluminum sulphate,  $Al_2(SO_4)_3$ .

3.6745	gm. salt gave	1.0965	$Al_2O_3$ .	29.841	per cent.
2.539	"	.7572	"	29.823	"
				<hr/>	
				Mean, 29.832,	$\pm .0061$

Hence  $Al = 26.858$ .

It is clear that the single determinations of Berzelius, Mather, Tissier, Isnard, and Terreil may now be safely left out of account, for the reason that none of them could affect appreciably the final value for  $Al$ . The ratios to consider are as follows:

- (1.)  $3Ag : AlCl_3 :: 100 : 41.344, \pm .0070$
- (2.) Percentage of  $Al_2O_3$  in ammonium alum, 11.2793,  $\pm .0008$
- (3.)  $3Ag : AlBr_3 :: 100 : 82.455, \pm .0010$
- (4.)  $H : Al :: 1 : 26.890, \pm .0034$
- (5.)  $Al_2 : 3H_2O :: 10 : 9.9818, \pm .0017$
- (6.) Percentage of  $Al_2O_3$  in  $Al_2(SO_4)_3$ , 29.832,  $\pm .0061$

The antecedent values are—

$O = 15.879, \pm .0003$	$Br = 79.344, \pm .0062$
$Ag = 107.108, \pm .0031$	$N = 13.935, \pm .0021$
$Cl = 35.179, \pm .0048$	$S = 31.828, \pm .0015$

\* Am. Chem. Journ., 10, 74. 1888.

† Compt. Rend., 97, 1369. 1883.



Hence for aluminum we have—

From (1).....	Al = 27.311, $\pm$ .0270
From (2).....	" = 26.952, $\pm$ .0037
From (3).....	" = 26.916, $\pm$ .0201
From (4).....	" = 26.890, $\pm$ .0034
From (5).....	" = 26.867, $\pm$ .0046
From (6).....	" = 26.858, $\pm$ .0113
General mean.....	Al = 26.906, $\pm$ .0021

With O = 16, Al = 27.111. The rejection of Dumas' data only lowers the result to 26.903.

## GALLIUM.

Gallium has been so recently discovered, and obtained in such small quantities, that its atomic weight has not as yet been determined with much precision. The following data were fixed by the discoverer, Lecoq de Boisbaudran :\*

3.1044 grammes gallium ammonium alum, upon ignition, left .5885 gm.  $\text{Ga}_2\text{O}_3$ .

Hence Ga = 69.595. If O = 16, Ga = 70.125.

.4481 grammes gallium, converted into nitrate and ignited, gave .6024 gm.  $\text{Ga}_2\text{O}_3$ .

Hence Ga = 69.171. If O = 16, Ga = 69.698.

These values, assigned equal weight, give these means :

With H = 1, Ga = 69.383.      With O = 16, Ga = 69.912

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\* Journ. Chem. Soc., 1878, p. 646.

## INDIUM.

Reich and Richter, the discoverers of indium, were also the first to determine its atomic weight.\* They dissolved weighed quantities of the metal in nitric acid, precipitated the solution with ammonia, ignited the precipitate, and ascertained its weight. Two experiments were made, as follows :

.5135	gram. indium gave	.6243	gram. $\text{In}_2\text{O}_3$ .
.699	“	.8515	“

Hence, in mean,  $\text{In} = 110.61$ , if  $\text{O} = 16$ ; a value known now to be too low.

An unweighed quantity of fresh, moist indium sulphide was also dissolved in nitric acid, yielding, on precipitation,

$$.2105 \text{ gram. } \text{In}_2\text{O}_3 \text{ and } .542 \text{ gram. } \text{BaSO}_4.$$

Hence, with  $\text{BaSO}_4 = 233.505$ ,  $\text{In} = 112.03$ ; also too low.

Soon after the publication of Reich and Richter's paper the subject was taken up by Winkler.† He dissolved indium in nitric acid, evaporated to dryness, ignited the residue, and weighed the oxide thus obtained.

.5574	gram. In gave	.6817	gram. $\text{In}_2\text{O}_3$ .
.6661	“	.8144	“
.5011	“	.6126	“

Hence, in mean, if  $\text{O} = 16$ ,  $\text{In} = 107.76$ ; a result even lower than the values already cited.

In a later paper by Winkler‡ better results were obtained. Two methods were employed. First, metallic indium was placed in a solution of pure, neutral, sodio-auric chloride, and the amount of gold precipitated was weighed. I give the weighings and, in a third column, the amount of indium proportional to 100 parts of gold :

<i>In.</i>	<i>Au.</i>	<i>Ratio.</i>
.4471 gram.	.8205 gram.	57.782
.8445 “	1.4596 “	57.858

Mean, 57.820,  $\pm .026$

Hence, if  $\text{Au} = 195.743$ ,  $\pm .0049$ ,  $\text{In} = 113.179$ ,  $\pm .0517$ .

Winkler also repeated his earlier process, converting indium into oxide by solution in nitric acid and ignition of the residue. An ad-

\* Journ. für Prakt. Chem., 92, 484.

† Journ. für Prakt. Chem., 94, 8.

‡ Journ. für Prakt. Chem., 102, 282.

ditional experiment, the third as given below, was made after the method of Reich and Richter. The third column gives the percentage of In in  $\text{In}_2\text{O}_3$ :

1.124	gram. In gave	1.3616	gram. $\text{In}_2\text{O}_3$ .	Per cent.,	82.550
1.015	"	1.2291	"	"	82.581
.6376	"	.7725	"	"	82.537

These figures were confirmed by a single experiment of Bunsen's,\* published simultaneously with the specific heat determinations which showed that the oxide of indium was  $\text{In}_2\text{O}_3$ , and not  $\text{InO}$ , as had been previously supposed:

1.0592 gram. In gave 1.2825 gram.  $\text{In}_2\text{O}_3$ . Per cent. In, 82.589

For convenience we may add this figure in with Winkler's series, which gives us a mean percentage of In in  $\text{In}_2\text{O}_3$  of  $82.564, \pm .0082$ . Hence, if  $\text{O} = 15.879, \pm .0003$ ,  $\text{In} = 112.787, \pm .0542$ .

Combining both values, we have—

From gold series, . . . . .	In =	113.179, $\pm .0517$
From oxide series, . . . . .	" =	112.787, $\pm .0542$
<hr/>		
General mean, . . . . .	In =	112.992, $\pm .0374$

If  $\text{O} = 16$ ,  $\text{In} = 113.853$ .

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\* Poggend. Annal., 141, 28.

## THALLIUM.

The atomic weight of this interesting metal has been fixed by the researches of Lamy, Werther, Hebbeling, Crookes, and Lepierre.

Lamy and Hebbeling investigated the chloride and sulphate; Werther studied the iodide; Crookes' experiments involved the synthesis of the nitrate. Lepierre's work is still more recent, and is based upon several compounds.

Lamy\* gives the results of one analysis of thallium sulphate and three of thallium chloride. 3.423 grammes  $\text{Tl}_2\text{SO}_4$  gave 1.578 gm.  $\text{BaSO}_4$ ; whence 100 parts of the latter are equivalent to 216.920 of the former. In the thallium chloride the chlorine was estimated as silver chloride. The following results were obtained. In the third column I give the amount of  $\text{TlCl}$  proportional to 100 parts of  $\text{AgCl}$ :

3.912	gram.	$\text{TlCl}$ gave	2.346	gram.	$\text{AgCl}$ .	166.752
3.000		"	1.8015		"	166.528
3.912		"	2.336		"	167.466

Mean, 166.915,  $\pm .1905$

Hebbeling's† work resembles that of Lamy. Reducing his weighings to the standards adopted above, we have from his sulphate series, as equivalent to 100 parts of  $\text{BaSO}_4$ , the amounts of  $\text{Tl}_2\text{SO}_4$  given in the third column:

1.4195	gram.	$\text{Tl}_2\text{SO}_4$ gave	.6534	gram.	$\text{BaSO}_4$ .	217.248
1.1924		"	.5507		"	216.524
.8560		"	.3957		"	216.325

Mean, 216.699

Including Lamy's single result as of equal weight, we get a mean of 216.754,  $\pm .1387$ .

From the chloride series we have these results, with the ratio stated as usual:

.2984	gram.	$\text{TlCl}$ gave	.1791	gram.	$\text{AgCl}$ .	166.611
.5452		"	.3278		"	166.321

Mean, 166.465,  $\pm .097$

Lamy's mean was 166.915,  $\pm .1905$ . Both means combined give a general mean of 166.555,  $\pm .0865$ .

Werther's‡ determinations of iodine in thallium iodide were made by two methods. In the first series  $\text{TlI}$  was decomposed by zinc and potassium hydroxide, and in the filtrate the iodine was estimated as  $\text{AgI}$ .

\* Zeit. Anal. Chem., 2, 211. 1863.

† Ann. Chem. Pharm., 134, 11. 1865.

‡ Journ. für Prakt. Chem., 92, 128. 1864.

One hundred parts of AgI correspond to the amounts of TII given in the last column :

.720	gram, TII gave	.51	gram, AgI,	141.176
2.072	"	1.472	"	140.761
.960	"	.679	"	141.384
.385	"	.273	"	141.026
1.068	"	.759	"	140.711

Mean, 141.012,  $\pm$  .085

In the second series the thallium iodide was decomposed by ammonia in presence of silver nitrate, and the resulting AgI was weighed. Expressed according to the foregoing standard, the results are as follows :

1.375	gram, TII gave	.978	gram, AgI,	Ratio, 140.593
1.540	"	1.095	"	" 140.639
1.380	"	.981	"	" 140.673

Mean, 140.635,  $\pm$  .016

General mean of both series, 140.648,  $\pm$  .016.

In 1873 Crookes,\* the discoverer of thallium, published his final determination of its atomic weight. His method was to effect the synthesis of thallium nitrate from weighed quantities of absolutely pure thallium. No precaution necessary to ensure purity of materials was neglected; the balances were constructed especially for the research; the weights were accurately tested and all their errors ascertained; weighings were made partly in air and partly in vacuo, but all were reduced to *absolute* standards; and unusually large quantities of thallium were employed in each experiment. In short, no effort was spared to attain as nearly as possible absolute precision of results. The details of the investigation are too voluminous, however, to be cited here; the reader who wishes to become familiar with them must consult the original memoir. Suffice it to say that the research is a model which other chemists will do well to copy.

The results of ten experiments by Professor Crookes may be stated as follows. In a final column I give the quantity of nitrate producible from 100 parts of thallium. The weights given are in grains :

<i>Thallium.</i>	<i>TlNO<sub>3</sub> + Glass.</i>	<i>Glass Vessel.</i>	<i>Ratio.</i>
497.972995	1121.851852	472.557319	130.3875
293.193507	1111.387014	729.082713	130.3930
288.562777	971.214142	594.949719	130.3926
324.963740	1142.569408	718.849078	130.3900
183.790232	1005.779897	766.133831	130.3912
190.842532	997.334615	748.491271	130.3920
195.544324	1022.176679	767.203451	130.3915
201.816345	1013.480135	750.332401	130.3897
295.683523	1153.947672	768.403621	130.3908
299.203036	1159.870052	769.734201	130.3917

Mean, 130.3910,  $\pm$  .00034

\* Phil. Trans., 1873, p. 277.

Lepierre's\* determinations were published in 1893, and represented several distinct methods. First, thalious sulphate was subjected to electrolysis in presence of an excess of ammonium oxalate, the reduced metal being dried and weighed in an atmosphere of hydrogen. The corrected weights, etc., are as follows :

1.8935	gram. $\text{Ti}_2\text{SO}_4$	gave 1.5327	Tl.	80.945	per cent.
2.7243	"	2.2055	"	80.957	"
2.8112	"	2.2759	"	80.958	"
					<hr/>
					Mean, 80.953, $\pm .0030$

Secondly, weighed quantities of crystallized thallic oxide were converted into thalious sulphate by means of sulphurous acid, and the solution was then subjected to electrolysis, as in the preceding series.

3.2216	gram. $\text{Ti}_2\text{O}_3$	gave 2.8829	Tl.	89.487	per cent.
2.5417	"	2.2742	"	89.475	"
					<hr/>
					Mean, 89.481, $\pm .0040$

In the third set of experiments a definite amount of thalious sulphate or nitrate was fused in a polished silver crucible with ten times its weight of absolutely pure caustic potash. Thallic oxide was thus formed, which, with various precautions, was washed with water and alcohol, and finally weighed in the original crucible. One experiment with the nitrate gave—

2.7591	gram. $\text{TiNO}_3$	yields 2.3649	$\text{Ti}_2\text{O}_3$ .	85.713	per cent.
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Two experiments were made with the sulphate, as follows :

3.1012	gram. $\text{Ti}_2\text{SO}_4$	gave 2.8056	$\text{Ti}_2\text{O}_3$ .	90.468	per cent.
2.3478	"	2.1239	"	90.463	"
					<hr/>
					Mean, 90.465, $\pm .0020$

Finally, crystallized thallic oxide was reduced by heat in a stream of hydrogen, and the water so formed was collected and weighed.

2.7873	gram. $\text{Ti}_2\text{O}_3$	gave .3301	$\text{H}_2\text{O}$ .	11.843	per cent.
3.9871	"	.4716	"	11.828	"
4.0213	"	.4761	"	11.839	"
					<hr/>
					Mean, 11.837, $\pm .0029$

In a supplementary note† Lepierre states that his weights were all reduced to vacuum standards.

Some work by Wells and Penfield, ‡ incidentally involving a determination of atomic weight, but primarily intended for another purpose, may also be taken into account. Their question was as to the constancy of thallium itself. The nitrate was repeatedly crystallized, and the last crystallization, with the mother liquor representing the opposite end of

\* Bull. Soc. Chim. (3), 9, 166.

† Bull. Soc. Chim. (3), 11, 423. 1894.

‡ Amer. Journ. Sci. (3), 47, 466. 1894.

the series, were both converted into chloride. In the latter the chlorine was estimated as silver chloride, which was weighed on a Gooch filter, with the results given below, which are sensibly identical. The  $\text{TlCl}$  equivalent to 100 parts of  $\text{AgCl}$  is stated in the last column.

	<i>TlCl.</i>	<i>AgCl.</i>	<i>Ratio.</i>
Crystals.....	3.9146	2.3393	167.341
Mother liquor.....	3.3415	1.9968	167.343
			<hr/> Mean, 167.342

The general mean of Lamy's and Hebbberling's determinations of this ratio gave  $166.555, \pm .0865$ . If we arbitrarily assign Wells and Penfield's mean equal weight with that, we get a new general mean of  $166.948, \pm .0610$ .

The ratios to be considered are now as follows:

- (1.)  $\text{BaSO}_4 : \text{Tl}_2\text{SO}_4 :: 100 : 216.754, \pm .1387$
- (2.)  $\text{AgCl} : \text{TlCl} :: 100 : 166.948, \pm .0610$
- (3.)  $\text{AgI} : \text{TlI} :: 100 : 140.648, \pm .016$
- (4.)  $\text{Tl} : \text{TlNO}_3 :: 100 : 130.391, \pm .00034$
- (5.)  $\text{Tl}_2\text{SO}_4 : \text{Tl}_2 :: 100 : 80.953, \pm .0030$
- (6.)  $\text{Tl}_2\text{O}_3 : \text{Tl}_2 :: 100 : 89.481, \pm .0040$
- (7.)  $2\text{TlNO}_3 : \text{Tl}_2\text{O}_3 :: 100 : 85.713$
- (8.)  $\text{Tl}_2\text{SO}_4 : \text{Tl}_2\text{O}_3 :: 100 : 90.465, \pm .0020$
- (9.)  $\text{Tl}_2\text{O}_3 : 3\text{H}_2\text{O} :: 100 : 11.837, \pm .0029$

And the antecedent data are these:

O = 15.879, $\pm .0003$	N = 13.935, $\pm .0021$
Ag = 107.108, $\pm .0031$	S = 31.828, $\pm .0015$
Cl = 35.179, $\pm .0048$	AgCl = 142.287, $\pm .0037$
I = 125.888, $\pm .0069$	AgI = 232.996, $\pm .0062$

Ratio number seven rests upon a single experiment, and the atomic weight of thallium derived from it must therefore be arbitrarily weighted. It has been assumed, therefore, that its probable error is the same as that from number eight. Taking this much for granted, we have nine values for thallium, as given below:

From (1) .....	Tl = 203.478, $\pm .1610$
From (2) .....	" = 202.366, $\pm .0872$
From (3) .....	" = 201.816, $\pm .0389$
From (4) .....	" = 202.595, $\pm .0117$
From (5) .....	" = 202.614, $\pm .0330$
From (6) .....	" = 202.620, $\pm .0775$
From (7) .....	" = 202.679, $\pm .0483$
From (8) .....	" = 202.496, $\pm .0483$
From (9) .....	" = 202.746, $\pm .0576$
<hr/>	
General mean .....	Tl = 202.555, $\pm .0098$

If O = 16, Tl = 204.098.

If we reject the first three values, retaining only those due to the experiments of Crookes and Lepierre, we have—

$$\text{Tl} = 202.605, \pm .0103$$

If  $\text{O} = 16$ , this becomes 204.149. This mean exceeds Crookes' determination only by 0.01, and may be regarded as fairly satisfactory. Crookes' ratio evidently outweighs all the others.

## SILICON.

Although Berzelius\* attempted to ascertain the atomic weight of silicon, first by converting pure Si into  $\text{SiO}_2$ , and later from the analysis of  $\text{BaSiF}_6$ , his results were not satisfactory. We need consider only the work of Pelouze, Schiel, Dumas, and Thorpe and Young.

Pelouze,† experimenting upon silicon tetrachloride, employed his usual method of titration with a solution containing a known weight of silver. One hundred parts of Ag gave the following equivalencies of  $\text{SiCl}_4$ :

$$\begin{array}{r} 39.4325 \\ 39.4570 \\ \hline \text{Mean, } 39.4447, \pm .0083 \end{array}$$

Essentially the same method was adopted by Dumas.‡ Pure  $\text{SiCl}_4$  was weighed in a sealed glass bulb, then decomposed by water, and titrated. The results for 100 Ag are given in the third column:

2.899 gm. $\text{SiCl}_4$	= 7.3558 gm. Ag.	39.411
1.242	" 3.154	39.379
3.221	" 8.1875	39.340
		<hr/>
		Mean, 39.377, $\pm .014$

Dumas' and Pelouze's series combine as follows:

Pelouze .....	39.4447, $\pm .0083$
Dumas .....	39.377, $\pm .014$
<hr/>	
General mean.....	39.4265, $\pm .0071$

Schiel,§ also studying the chloride of silicon, decomposed it by ammonia. After warming and long standing it was filtered, and in the

\* Lehrbuch, 5 Aufl., 3, 1200.

† Compt. Rend., 20, 1047. 1845.

‡ Ann. Chem. Pharm., 113, 31. 1860.

§ Ann. Chem. Pharm., 120, 94.



filtrate the chlorine was estimated as AgCl. One hundred parts of AgCl correspond to the quantities of  $\text{SiCl}_4$  given in the last column :

.6738	gram.	$\text{SiCl}_4$	gave	2.277	gram.	AgCl.	29.592
1.3092		"		4.418		"	29.633
							<hr/>
Mean,							29.6125, $\pm .0138$

Thorpe and Young,\* working with silicon bromide, seem to have obtained fairly good results. The bromide was perfectly clear and colorless, and boiled constantly at  $153^\circ$ . It was weighed, decomposed with water, and evaporated to dryness, the crucible containing it being finally ignited. The crucible was tared by one precisely similar, in which an equal volume of water was also evaporated. Results as follows, with weights at vacuum standards:

9.63007	gram.	$\text{SiBr}_4$	gave	1.67070	$\text{SiO}_2$ .	17.349	per cent.
12.36099		"		2.14318	"	17.338	"
12.98336		"		2.25244	"	17.349	"
9.02269		"		1.56542	"	17.350	"
15.38426		"		2.66518	"	17.324	"
9.74550		"		1.69020	"	17.343	"
6.19159		"		1.07536	"	17.368	"
9.51204		"		1.65065	"	17.353	"
10.69317		"		1.85555	"	17.353	"
							<hr/>
Mean,							17.347, $\pm .0027$

The ratios now available are—

- (1.)  $4\text{Ag} : \text{SiCl}_4 :: 100 : 39.4265, \pm .0071$
- (2.)  $4\text{AgCl} : \text{SiCl}_4 :: 100 : 29.6125, \pm .0138$
- (3.)  $\text{SiBr}_4 : \text{SiO}_2 :: 100 : 17.347, \pm .0027$

Reducing these ratios with—

O = 15.879, $\pm .0003$	Br = 79.344, $\pm .0062$
Ag = 107.108, $\pm .0031$	AgCl = 142.287, $\pm .0037$ ,
Cl = 35.179, $\pm .0048$	

we have the following values for the atomic weight of silicon :

From (1) .....	Si = 28.200, $\pm .0363$
From (2) .....	" = 27.823, $\pm .0810$
From (3) .....	" = 28.187, $\pm .0122$
<hr/>	
General mean .....	Si = 28.181, $\pm .0114$

If O = 16, Si = 28.395.

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\* Journ. Chem. Soc., 51, 576. 1887.

## TITANIUM.

The earliest determinations of the atomic weight of titanium are due to Heinrich Rose.\* In his first investigation he studied the conversion of titanium sulphide into titanous acid, and obtained erroneous results; later, in 1829, he published his analyses of the chloride.† This compound was purified by repeated rectifications over mercury and over potassium, and was weighed in bulbs of thin glass. These were broken under water in tightly stoppered flasks; the titanous acid was precipitated by ammonia, and the chlorine was estimated as silver chloride. The following results were obtained. In a fourth column I give the  $\text{TiO}_2$  in percentages referred to  $\text{TiCl}_4$  as 100, and in a fifth column the quantity of  $\text{TiCl}_4$  proportional to 100 parts of  $\text{AgCl}$ :

$\text{TiCl}_4$ .	$\text{TiO}_2$ .	$\text{AgCl}$ .	Per cent. $\text{TiO}_2$ .	$\text{AgCl}$ Ratio.
.885 grm.	.379 grm.	2.661 grm.	42.825	33.258
2.6365 "	1.120 "	7.954 "	42.481	33.147
1.7157 "	.732 "	5.172 "	42.665	33.173
3.0455 "	1.322 "	9.198 "	43.423	33.100
2.4403 "	1.056 "	7.372 "	43.273	33.102
Mean, 42.933, $\pm .121$				33.156, $\pm .019$

If we directly compare the  $\text{AgCl}$  with the  $\text{TiO}_2$  we shall find 100 parts of the former proportional to the following quantities of the latter:

14.243
14.081
14.153
14.373
14.324
Mean, 14.235, $\pm .036$

Shortly after the appearance of Rose's paper, Mosander‡ published some figures giving the percentage of oxygen in titanium dioxide, from which a value for the atomic weight of titanium was deduced. Although no details are furnished as to experimental methods, and no actual weighings are given, I cite his percentages for whatever they may be worth:

40.814
40.825
40.610
40.180
40.107
40.050
40.780
40.660
39.830
Mean, 40.428

\* Gilbert's Annalen; 1823, 67 and 129.

† Poggend. Annalen, 15, 145. Berz. Lehrbuch, 3, 1210.

‡ Berz. Jahresbericht, 10, 108. 1831.

These figures, with  $O = 15.879$ , give values for  $Ti$  ranging from 46.03 to 47.98; or, in mean,  $Ti = 46.80$ . They are not, however, sufficiently explicit to deserve any farther consideration.

In 1847 Isidor Pierre made public a series of important determinations.\* Titanium chloride, free from silicon and from iron, was prepared by the action of chlorine upon a mixture of carbon with pure, artificial titanous acid. This chloride was weighed in sealed tubes, these were broken under water, and the resulting hydrochloric acid was titrated with a standard solution of silver after the method of Pelouze. I subjoin Pierre's weighings, and add, in a third column, the ratio of  $TiCl_4$  to 100 parts of silver:

$TiCl_4$ .	<i>Ag.</i>	<i>Ratio.</i>
.8215 grm.	1.84523 grm.	44.520
.7740 "	1.73909 "	44.506
.7775 "	1.74613 "	44.527
.7160 "	1.61219 "	44.412
.8085 "	1.82344 "	44.339
.6325 "	1.42230 "	44.470
.8155 "	1.83705 "	44.392
.8165 "	1.83899 "	44.399
.8065 "	1.81965 "	44.322

Mean, 44.432,  $\pm .0173$

It will be seen that the first three of these results agree well with each other and are much higher than the remaining six. The last four experiments were made purposely with tubes which had been previously opened, in order to determine the cause of the discrepancy. According to Pierre, the opening of a tube of titanium chloride admits a trace of atmospheric moisture. This causes a deposit of titanous acid near the mouth of the tube, and liberates hydrochloric acid. The latter gas being heavy, a part of it falls back into the tube, so that the remaining chloride is richer in chlorine and poorer in titanium than it should be. Hence, upon titration, too low figures for the atomic weight of titanium are obtained. Pierre accordingly rejects all but the first three of the above estimations.

The memoir of Pierre upon the atomic weight of titanium was soon followed by a paper from Demoly, † who obtained much higher results. He also started out from titanous chloride, which was prepared from rutile. The latter substance was found to contain 1.8 per cent. of silica; whence Demoly inferred that the  $TiCl_4$  investigated by Rose and by Pierre might have been contaminated with  $SiCl_4$ , an impurity which would lower the value deduced for the atomic weight under consideration. Accordingly, in order to eliminate all such possible impurities, this process was resorted

\* Ann. Chim. Phys. (3), 20, 257.

† Ann. Chem. Pharm., 72, 214. 1849.

to: the chloride, after rectification over mercury and potassium, was acted upon by dry ammonia, whereupon the compound  $\text{TiCl}_4 \cdot 4\text{NH}_3$  was deposited as a white powder. This was ignited in dry ammonia gas, and the residue, by means of chlorine, was reconverted into titanous chloride, which was again repeatedly rectified over mercury, potassium, and potassium amalgam. The product boiled steadily at  $135^\circ$ . This chloride, after weighing in a glass bulb, was decomposed by water, the titanous acid was precipitated by ammonia, and the chlorine was estimated in the filtrate as silver chloride. Three analyses were performed, yielding the following results. I give the actual weighings:

1.470 grm.	$\text{TiCl}_4$	gave	4.241 grm.	$\text{AgCl}$	and	.565 grm.	$\text{TiO}_2$
2.330	"		6.752	"		.801	"
2.880	"		8.330	"		1.088	"

The ".801" in the last column is certainly a misprint for .901. Assuming this correction, the results may be given in three ratios, thus:

<i>Per cent. <math>\text{TiO}_2</math> from <math>\text{TiCl}_4</math>.</i>	<i><math>\text{TiCl}_4 : 100 \text{AgCl}</math>.</i>	<i><math>\text{TiO}_2 : 100 \text{AgCl}</math>.</i>
38.435	34.662	13.322
38.669	34.508	13.344
37.778	34.574	13.061
<hr/> Mean, 38.294, $\pm .180$	<hr/> 34.581, $\pm .030$	<hr/> 13.242, $\pm .061$

These three ratios give three widely divergent values for the atomic weight of titanium, ranging from about 36 to more than 56, the latter figure being derived from the ratio between  $\text{AgCl}$  and  $\text{TiCl}_4$ . This value, 56, is assumed by Demoly to be the best, the others being practically ignored.

Upon comparing Demoly's figures with those obtained by Rose, certain points of similarity are plainly to be noted. Both sets of results were reached by essentially the same method, and in both the discordance between the percentages of titanous acid and of silver chloride is glaring. This discordance can rationally be accounted for by assuming that the titanous chloride was in neither case absolutely what it purported to be; that, in brief, it must have contained impurities, such for example as hydrochloric acid, as shown in the experiments of Pierre, or possibly traces of oxychlorides. Considerations of this kind also throw doubt upon the results attained by Pierre, for he neglected the direct estimation of the titanous acid altogether, thus leaving us without means for correctly judging as to the character of his material.

In 1883\* Thorpe published a series of experiments upon titanium tetrachloride, determining three distinct ratios and getting sharply concordant results. The first ratio, which was essentially like Pierre's, by

\* Berichte Deutsch. Chem. Gesell., 16, 3014. 1883.

decomposition with water and titration with silver, was in detail as follows :

<i>TiCl<sub>4</sub></i> .	<i>Ag.</i>	<i>TiCl<sub>4</sub> : 100Ag.</i>
2.43275	5.52797	44.008
5.42332	12.32260	44.015
3.59601	8.17461	44.000
3.31222	7.52721	44.003
4.20093	9.54679	44.004
5.68888	12.92686	44.008
5.65346	12.85490	43.979
4.08247	9.28305	43.978
		Mean, 43.999, $\pm$ .0032
		Pierre found, 44.432, $\pm$ .0073
		General mean, 44.017, $\pm$ .0031

The second ratio, which involved the weights of  $TiCl_4$  taken in the last five determinations of the preceding series, included the weighing of the silver chloride formed. The  $TiCl_4$  proportional to 100 parts of  $AgCl$  is given in a third column :

<i>TiCl<sub>4</sub></i> .	<i>AgCl.</i>	<i>Ratio.</i>
3.31222	10.00235	33.114
4.20093	12.68762	33.111
5.68888	17.17842	33.117
5.65346	17.06703	33.125
4.08247	12.32442	33.125
		Mean, 33.118, $\pm$ .0019
		Rose found, 33.156, $\pm$ .019
		Demoly found, 34.581, $\pm$ .030
		General mean, 33.123, $\pm$ .0019.

In the third series the chloride was decomposed by water, and after evaporation to dryness the resulting  $TiO_2$  was strongly ignited.

<i>TiCl<sub>4</sub></i> .	<i>TiO<sub>2</sub></i> .	<i>Per cent. TiO<sub>2</sub></i> .
6.23398	2.62825	42.160
8.96938	3.78335	42.181
10.19853	4.30128	42.176
6.56894	2.77011	42.170
8.99981	3.79575	42.176
8.32885	3.51158	42.162
		Mean, 42.171, $\pm$ .0022
		Rose found, 42.933, $\pm$ .121
		Demoly found, 38.294, $\pm$ .180
		General mean, 42.171, $\pm$ .0022

In short, the work of Rose, Pierre, and Demoly practically vanishes. Furthermore, as will be seen later, the three ratios now give closely

agreeing values for the atomic weight of titanium. The cross ratio,  $4\text{AgCl} : \text{TiO}_2$  is not directly given by either of Thorpe's series; but the data furnished by Rose and Demoly combine into a general mean of  $4\text{AgCl} : \text{TiO}_2 :: 100 : 13.980, \pm .0303$ .

Some two years later Thorpe published his work more in detail,\* and added a set of determinations, like those made upon the chloride, in which titanium tetrabromide was studied. Three ratios were measured, as was the case with the chloride. In the first, the bromide was decomposed by water and titrated with a silver solution.

<i>TiBr<sub>4</sub>.</i>	<i>Ag.</i>	<i>TiBr<sub>4</sub> : 100.Ag.</i>
2.854735	3.34927	85.235
3.120848	3.66122	85.241
4.731118	5.55097	85.230
6.969075	8.17645	85.234
6.678099	7.83493	85.234
		Mean, 85.235, $\pm .0027$

In the four last experiments of the preceding series, the silver bromide formed was weighed. The third column gives the  $\text{TiBr}_4$  proportional to 100 parts of  $\text{AgBr}$ .

<i>TiBr<sub>4</sub>.</i>	<i>AgBr.</i>	<i>Ratio.</i>
3.120848	6.375391	48.951
4.731118	9.663901	48.957
6.969075	14.227716	48.982
6.678099	13.639956	48.959
		Mean, 48.962, $\pm .0049$

For the third ratio the bromide was decomposed by water; and after evaporation with ammonia the residual titanic oxide was ignited and weighed:

<i>TiBr<sub>4</sub>.</i>	<i>TiO<sub>2</sub>.</i>	<i>Per cent. TiO<sub>2</sub>.</i>
6.969730	1.518722	21.790
8.836783	1.923609	21.768
9.096309	1.979513	21.762
		Mean, 21.773, $\pm .0062$

Ignoring Mosander's work as unavailable, we have the following ratios to consider:

- (1.)  $4\text{Ag} : \text{TiCl}_4 :: 100 : 44.017, \pm .0031$
- (2.)  $4\text{AgCl} : \text{TiCl}_4 :: 100 : 33.123, \pm .0019$
- (3.)  $4\text{AgCl} : \text{TiO}_2 :: 100 : 13.980, \pm .0303$
- (4.)  $\text{TiCl}_4 : \text{TiO}_2 :: 100 : 42.171, \pm .0022$
- (5.)  $4\text{Ag} : \text{TiBr}_4 :: 100 : 85.235, \pm .0027$
- (6.)  $4\text{AgBr} : \text{TiBr}_4 :: 100 : 48.962, \pm .0049$
- (7.)  $\text{TiBr}_4 : \text{TiO}_2 :: 100 : 21.773, \pm .0062$

\* Journ. Chem. Soc., Feb., 1835, p. 108, and March, p. 129.

These are to be computed with—

O = 15.879, $\pm$ .0003	Br = 79.344, $\pm$ .0062
Ag = 107.108, $\pm$ .0031	AgCl = 142.287, $\pm$ .0037
Cl = 35.179, $\pm$ .0048	AgBr = 186.454, $\pm$ .0054

For the molecular weight of titanium chloride they give two values :

From (1) .....	TiCl <sub>4</sub> = 188.583, $\pm$ .0144
From (2) .....	“ = 188.519, $\pm$ .0119
General mean .....	TiCl <sub>4</sub> = 188.545, $\pm$ .0092

For TiBr<sub>4</sub> we have—

From (5) .....	TiBr <sub>4</sub> = 365.174, $\pm$ .0157
From (6) .....	“ = 365.163, $\pm$ .0380
General mean .....	TiBr <sub>4</sub> = 365.172, $\pm$ .0145

And for the atomic weight of titanium five values are calculable, as follows :

From molecular weight of TiCl <sub>4</sub> .....	Ti = 47.829, $\pm$ .0213
From molecular weight of TiBr <sub>4</sub> .....	“ = 47.796, $\pm$ .0260
From (3) .....	“ = 47.809, $\pm$ .1725
From (4) .....	“ = 47.698, $\pm$ .0268
From (7) .....	“ = 47.738, $\pm$ .0787
General mean .....	Ti = 47.786, $\pm$ .0138

If O = 16, this becomes Ti = 48.150.

## GERMANIUM.

The data relative to the atomic weight of germanium are rather scanty, and are due entirely to the discoverer of the element, Winkler.\* The pure tetrachloride was decomposed by sodium carbonate, mixed with a known excess of standard silver solution, and then titrated back with ammonium sulphocyanate. The data given are as follows :

<i>GeCl<sub>4</sub>.</i>	<i>Cl Found.</i>	<i>Per cent. Cl.</i>
.1067	.076112	66.177
.1258	.083212	66.146
.2223	.147136	66.188
.2904	.192190	66.182
		Mean, 66.173

Hence, with Cl = 35.179, Ge = 71.933. If O = 16, Ge = 72.481.

\* Journ. für Prakt. Chem. (2), 34, 177. 1886.

## ZIRCONIUM.

The atomic weight of zirconium has been determined by Berzelius, Hermann, Marignac, Weibull, and Bailey. Berzelius\* ignited the neutral sulphate, and thus ascertained the ratio in it between the  $\text{ZrO}_2$  and the  $\text{SO}_3$ . Putting  $\text{SO}_3$  at 100, he gives the following proportional quantities of  $\text{ZrO}_2$ :

75.84
75.92
75.80
75.74
75.97
75.85

Mean, 75.853,  $\pm .023$

This gives 43.134,  $\pm .0142$  as the percentage of zirconia in the sulphate.

Hermann's† estimate of the atomic weight of zirconium was based upon analyses of the chloride, concerning which he gives no details nor weighings. From sublimed zirconium chloride he finds  $\text{Zr} = 831.8$ , when  $\text{O} = 100$ ; and from two lots of the basic chloride  $2\text{ZrOCl}_2 \cdot 9\text{H}_2\text{O}$ ,  $\text{Zr} = 835.65$  and  $851.40$  respectively. The mean of all three is 839.62; whence, with modern formulæ and  $\text{O} = 15.879$ ,  $\text{Zr}$  becomes  $= 88.882$ .

Marignac's results‡ were obtained by analyzing the double fluoride of zirconium and potassium. His weights are as follows:

1.000	gram.	gave	.431	gram.	$\text{ZrO}_2$	and	.613	gram.	$\text{K}_2\text{SO}_4$ .
2.000	"		.864	"			1.232	"	
.654	"		.282	"			.399	"	
5.000	"		2.169	"			3.078	"	

These figures give us three ratios. A, the  $\text{ZrO}_2$  from 100 parts of salt; B, the  $\text{K}_2\text{SO}_4$  from 100 parts of salt; and C, the  $\text{ZrO}_2$  proportional to 100 parts of  $\text{K}_2\text{SO}_4$ :

A.	B.	C.
43.100	61.300	70.310
43.200	61.600	70.130
43.119	61.000	70.677
43.380	61.560	70.468
Mean, 43.200, $\pm .043$	Mean, 61.365, $\pm .094$	Mean, 70.396, $\pm .079$ .

Weibull,§ following Berzelius, ignited the sulphate, and also made a

\* Poggend. Annal, 4, 126. 1825.

† Journ. für Prakt. Chem., 31, 77. Berz. Jahresb., 25, 147.

‡ Ann. Chim. Phys. (3), 60, 270. 1860.

§ Lund. Arsskrift, v. 18. 1881-'82.



similar set of experiments with the selenate of zirconium, obtaining results as follows :

*Sulphate.*  $Zr(SO_4)_2$ .

1.5499	gram. salt gave	.6684	$ZrO_2$ ,	43.126	per cent.
1.5445	"	.6665	"	43.153	"
2.1683	"	.9360	"	43.168	"
1.0840	"	.4670	"	43.081	"
.7913	"	.3422	"	43.321	"
.6251	"	.2695	"	43.113	"
.4704	"	.2027	"	43.091	"

Mean, 43.150,  $\pm$  .0207

*Selenate.*  $Zr(SeO_4)_2$ .

1.0212	gram. salt gave	.3323	$ZrO_2$ ,	32.540	per cent.
.8418	"	.2744	"	32.597	"
.6035	"	.1964	"	32.544	"
.8793	"	.2870	"	32.640	"
.3089	"	.1003	"	32.470	"

Mean, 32.558,  $\pm$  .0192

Bailey \* also ignited the sulphate, after careful investigation of his material, and of the conditions needful to ensure success. He found that the salt was perfectly stable at  $400^\circ$ , while every trace of free sulphuric acid was expelled at  $350^\circ$ . The chief difficulty in the process arises from the fact that the zirconia produced by the ignition is very light, and easily carried off mechanically, so that the percentage found is likely to be too low. This difficulty was avoided by the use of a double crucible, the outer one retaining particles of zirconia which otherwise might be lost. The results, corrected for buoyancy of the air, are as follows :

2.02357	salt gave	.87785	$ZrO_2$ ,	43.381	per cent.
2.6185	"	1.1354	"	43.360	"
2.27709	"	.98713	"	43.350	"
2.21645	"	.96152	"	43.385	"
1.75358	"	.76107	"	43.402	"
1.64065	"	.7120	"	43.397	"
2.33255	"	1.01143	"	43.361	"
1.81105	"	.78485	"	43.337	"

Mean, 43.372,  $\pm$  .0056

This, combined with previous determinations, gives—

Berzelius	.....	43.134, $\pm$ .0142
Weibull	.....	43.150, $\pm$ .0207
Bailey	.....	43.372, $\pm$ .0056

General mean ..... 43.317,  $\pm$  .0051

\* Proc. Roy. Soc., 46, 74. Chem. News, 60, 32.

For computing the atomic weight of zirconium we now have the sub-joined ratios:

- (1.) Percentage  $\text{ZrO}_2$  in  $\text{Zr}(\text{SO}_4)_2$ ,  $43.317, \pm .0051$
- (2.) Percentage  $\text{ZrO}_2$  in  $\text{Zr}(\text{SeO}_4)_2$ ,  $32.558, \pm .0192$
- (3.) Percentage  $\text{ZrO}_2$  from  $\text{K}_2\text{ZrF}_6$ ,  $43.200, \pm .043$
- (4.) Percentage  $\text{K}_2\text{SO}_4$  from  $\text{K}_2\text{ZrF}_6$ ,  $61.365, \pm .094$
- (5.)  $\text{K}_2\text{SO}_4 : \text{ZrO}_2 :: 100 : 70.396, \pm .079$

The antecedent atomic weights are—

O = 15.879, $\pm .0003$	K = 38.817, $\pm .0051$
S = 31.828, $\pm .0015$	F = 18.912, $\pm .0029$
Se = 78.419, $\pm .0042$	

With these data we first get three values for the molecular weight of zirconia:

From (1) .....	$\text{ZrO}_2 = 121.454, \pm .0182$
From (2) .....	“ = $121.708, \pm .0798$
From (5) .....	“ = $121.770, \pm .1370$
<hr/>	
General mean .....	$\text{ZrO}_2 = 121.471, \pm .0176$

Finally, there are three independent estimates for the atomic weight of zirconium:

From molecular weight $\text{ZrO}_2$ .....	Zr = $89.713, \pm .0177$
From ratio (3) .....	“ = $89.437, \pm .2390$
From ratio (4) .....	“ = $90.778, \pm .4326$
<hr/>	
General mean .....	Zr = $89.716, \pm .0175$

If O = 16, Zr = 90.400.

Here the first value alone carries appreciable weight.

## TIN.

The atomic weight of tin has been determined by means of the oxide, the chloride, the bromide, the sulphide, and the stannichlorides of potassium and ammonium.

The composition of stannic oxide has been fixed in two ways: by synthesis from the metal and by reduction in hydrogen. For the first method we may consider the work of Berzelius, Mulder and Vlaanderen, Dumas, Van der Plaats, and Bongartz and Classen.

Berzelius\* oxidized 100 parts of tin by nitric acid, and found that 127.2 parts of  $\text{SnO}_2$  were formed.

The work done by Mulder and Vlaanderen† was done in connection with a long investigation into the composition of Banca tin, which was found to be almost absolutely pure. For the atomic weight determinations, however, really pure tin was taken prepared from pure tin oxide. This metal was oxidized, by nitric acid, with the following results. 100 parts of tin gave of  $\text{SnO}_2$ :

127.56—Mulder.
127.56—Vlaanderen.
127.43—Vlaanderen.

Mean, 127.517,  $\pm .029$

Dumas‡ oxidized pure tin by nitric acid in a flask of glass. The resulting  $\text{SnO}_2$  was strongly ignited, first in the flask and afterwards in platinum. His weighings, reduced to the foregoing standard, give for dioxide from 100 parts of tin the amounts stated in the third column:

12.443	grm. Sn gave	15.820	grm. $\text{SnO}_2$ .	127.14
15.976	"	20.301	"	127.07

Mean, 127.105,  $\pm .024$

In an investigation later than that previously cited, Vlaanderen§ found that when tin was oxidized in glass or porcelain vessels, and the resulting oxide ignited in them, traces of nitric acid were retained. When, on the other hand, the oxide was strongly heated in platinum, the latter was perceptibly attacked, so much so as to render the results uncertain. He therefore, in order to fix the atomic weight of tin, reduced the oxide by heating it in a porcelain boat in a stream of hydrogen. Two experiments gave  $\text{Sn} = 118.08$ , and  $\text{Sn} = 118.24$ . These, when  $\text{O} = 16$ , become, if reduced to the above common standard,

\* Poggend. Annal., 8, 177.

† Journ. für Prakt. Chem., 49, 35. 1849.

‡ Ann. Chem. Pharm., 113, 26.

§ Jahresbericht, 1858, 183.

$$\begin{array}{r}
 127.100 \\
 127.064 \\
 \hline
 \text{Mean, } 127.082, \pm .012
 \end{array}$$

Van der Plaats\* prepared pure stannic oxide from East Indian tin (Banca), and upon the material obtained made two series of experiments; one by reduction and one by oxidation. The results, with vacuum weights, are as follows, the ratio between Sn and SnO<sub>2</sub> appearing in the third column:

*Oxidation Series.*

9.6756	gram. tin gave	12.2967	SnO <sub>2</sub> .	127.091
12.7356	"	16.1885	"	127.114
23.4211	"	29.7667	"	127.093

*Reduction Series.*

5.5015	gram. SnO <sub>2</sub> gave	4.3280	tin.	127.114
4.9760	"	3.9145	"	127.117
3.8225	"	3.0078	"	127.086
2.9935	"	2.3553	"	127.096

Mean of both series as one, 127.102,  $\pm$  .0033

The reductions were effected in a porcelain crucible.

Bongartz and Classen† purified tin by electrolysis, and oxidized the electrolytic metal by means of nitric acid. The oxide found was dried over a water-bath, then heated over a weak flame, and finally ignited for several hours in a gas-muffle. Some reduction experiments gave values which were too low. The oxidation series was as follows, with the usual ratio added by me in a third column:

<i>Sn.</i>	<i>SnO<sub>2</sub>.</i>	<i>Ratio.</i>
2.5673	3.2570	126.865
3.8414	4.8729	126.852
7.3321	9.2994	126.831
5.4367	6.8962	126.845
7.3321	9.2994	126.831
9.8306	12.4785	126.935
11.2424	14.2665	126.896
5.5719	7.0685	126.860
9.8252	12.4713	126.932
4.3959	5.5795	126.925
6.3400	8.0440	126.877

Mean, 126.877,  $\pm$  .0080

We now have six series of experiments showing the amount of SnO<sub>2</sub> formed from 100 parts of tin. To Berzelius' single determination may be assigned the weight of one experiment in Mulder and Vlaanderen's series:

\* Compt. Rend., 100, 52 1885.

† Berichte Deutsch. Chem. Gesell., 21, 2900. 1888.

Berzelius.....	127.200, $\pm$ .041
Mulder and Vlaanderen.....	127.517, $\pm$ .029
Dumas .....	127.105, $\pm$ .024
Vlaanderen .....	127.082, $\pm$ .012
Van der Plaats.....	127.102, $\pm$ .0033
Bongartz and Classen.....	126.877, $\pm$ .0080
General mean .....	127.076, $\pm$ .0026

Dumas, in the paper previously quoted, also gives the results of some experiments with stannic chloride,  $\text{SnCl}_4$ . This was titrated with a solution containing a known weight of silver. From the weighings given, 100 parts of silver correspond to the quantities of  $\text{SnCl}_4$  named in the third column:

1.839 grm. $\text{SnCl}_4$ = 3.054 grm. Ag.	60.216
2.665        "        4.427        "	60.199
	Mean, 60.207, $\pm$ .006

Tin tetrabromide and the stannichlorides of potassium and ammonium were all studied by Bongartz and Classen; who, in each compound, carefully purified, determined the tin electrolytically. The data given are as follows, the percentage columns being added by myself:

*Tin Tetrabromide.*

$\text{SnBr}_4$ Taken.	$\text{Sn}$ Found.	Per cent. $\text{Sn}$ .
8.5781	2.3270	27.127
9.5850	2.6000	27.126
9.9889	2.7115	27.145
10.4914	2.8445	27.113
16.8620	4.5735	27.123
16.6752	4.5236	27.119
11.1086	3.0125	27.116
10.6356	2.8840	27.113
11.0871	3.0060	27.123
19.5167	5.2935	27.128
		Mean, 27.123, $\pm$ .0020

*Potassium Stannichloride.*

$\text{K}_2\text{SnCl}_6$ .	$\text{Sn}$ Found.	Per cent. $\text{Sn}$ .
2.5718	.7472	29.054
2.2464	.6524	29.042
9.3353	2.7100	29.030
12.1525	3.5285	29.035
12.4223	3.6070	29.036
15.0870	4.3812	29.040
10.4465	3.0330	29.034
18.9377	5.5029	29.058
18.4743	5.3630	29.029
17.6432	5.1244	29.045
		Mean, 29.040, $\pm$ .0021

*Ammonium Stannichloride.*

<i>Am<sub>2</sub>SnCl<sub>6</sub>.</i>	<i>Sn Found.</i>	<i>Per cent. Sn.</i>
1.6448	.5328	32.393
1.8984	.6141	32.347
2.0445	.6620	32.381
2.0654	.6690	32.391
2.0058	.6496	32.386
2.4389	.7895	32.371
4.0970	1.3254	32.351
3.4202	1.1078	32.390
3.6588	1.1836	32.349
1.5784	.5108	32.362
7.3248	2.3710	32.370
13.1460	4.2528	32.351
11.9483	3.8650	32.348
18.4747	5.9788	32.362
18.6635	6.0415	32.371
17.8894	5.7923	32.378

Mean, 32.369,  $\pm$  .0088

One other method of determination for the atomic weight of tin was employed by Bongartz and Classen. Electrolytic tin was converted into sulphide, and the sulphur so taken up was oxidized by means of hydrogen peroxide, by Classen's method, and weighed as barium sulphate. The results, as given by the authors, are subjoined :

<i>Sn Taken.</i>	<i>Per cent. of S Gained.</i>
2.6285	53.91
.7495	53.87
1.4785	53.94
2.5690	53.94
2.1765	53.85
1.3245	53.88
.9897	53.83
2.7160	53.86

Mean, 53.885,  $\pm$  .0098

This percentage of sulphur, however, was computed from weighings of barium sulphate. What values were assigned to the atomic weights of barium and sulphur is not stated, but as Meyer and Seubert's figures are used for other elements throughout this paper, we may assume that they apply here also. Putting O = 15.96, S = 31.98, and Ba = 136.86, the 53.885 per cent. of sulphur becomes 392.056,  $\pm$  .0713 of BaSO<sub>4</sub>, the compound actually weighed. This gives us the ratio—

$$\text{Sn} : 2\text{BaSO}_4 :: 100 : 392.056, \pm .0713$$

as the real result of the experiments, from which, with the later values for Ba, S, and O, the atomic weight of tin may be calculated.

We now have, for tin, the following available ratios :

- (1.)  $\text{Sn} : \text{SnO}_2 :: 100 : 127.076, \pm .0026$
- (2.)  $4\text{Ag} : \text{SnCl}_4 :: 100 : 60.207, \pm .0060$
- (3.) Percentage of tin in  $\text{SnBr}_4$ ,  $27.123, \pm .0020$
- (4.) Percentage of tin in  $\text{K}_2\text{SnCl}_6$ ,  $29.040, \pm .0021$ .
- (5.) Percentage of tin in  $\text{Am}_2\text{SnCl}_6$ ,  $32.369, \pm .0088$
- (6.)  $\text{Sn} : 2\text{BaSO}_4 :: 100 : 392.056, \pm .0713$

The antecedent values are—

O = 15.879, $\pm .0003$	K = 38.817, $\pm .0051$
Ag = 107.108, $\pm .0031$	N = 13.935, $\pm .0021$
Cl = 35.179, $\pm .0048$	S = 31.828, $\pm .0015$
Br = 79.344, $\pm .0062$	Ba = 136.392, $\pm .0086$

With these, six independent values for Sn are computable, as follows :

From (1).....	Sn = 117.292, $\pm .0115$
From (2).....	" = 117.230, $\pm .0331$
From (3).....	" = 118.120, $\pm .0131$
From (4).....	" = 118.152, $\pm .0155$
From (5).....	" = 118.190, $\pm .0382$
From (6).....	" = 118.216, $\pm .0220$
General mean.....	Sn = 117.805, $\pm .0069$

If  $O = 16$ ,  $\text{Sn} = 118.701$ .

If we reject the first two of these values, which include all of the older work, and take only the last four, which represent the concordant results of Bongartz and Classen, the general mean becomes—

$$\text{Sn} = 118.150, \pm .0089$$

Or, with  $O = 16$ ,  $\text{Sn} = 119.050$ . This mean I regard as having higher probability than the other.

A single determination of the atomic weight of tin, made by Schmidt,\* ought not to be overlooked, although it was only incidental to his research upon tin sulphide. In one experiment, 0.5243 gm. Sn gave 0.6659  $\text{SnO}_2$ . Hence, with  $O = 16$ ,  $\text{Sn} = 118.49$ . This lies about midway between the two sets of values already computed.

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\* Berichte, 27, 2743. 1894.

## THORIUM.

The atomic weight of thorium has been determined from analyses of the sulphate, oxalate, formate, and acetate, with widely varying results. The earliest figures are due to Berzelius,\* who worked with the sulphate, and with the double sulphate of potassium and thorium. The thorium was precipitated by ammonia, and the sulphuric acid was estimated as  $\text{BaSO}_4$ . The sulphate gave the following ratios in two experiments. The third column represents the weight of  $\text{ThO}_2$  proportional to 100 parts of  $\text{BaSO}_4$ :

.6754 grm.	$\text{ThO}_2 = 1.159$ grm.	$\text{BaSO}_4$ .	Ratio, 58.274
1.0515	"	1.832	" 57.396

The double potassium sulphate gave .265 grm.  $\text{ThO}_2$ , .156 grm.  $\text{SO}_3$ , and .3435  $\text{K}_2\text{SO}_4$ . The  $\text{SO}_3$ , with the Berzelian atomic weights, represents .4537 grm.  $\text{BaSO}_4$ . Hence 100  $\text{BaSO}_4$  is equivalent to 58.408  $\text{ThO}_2$ . This figure, combined with the two previous values for the same ratio, gives a mean of 58.026,  $\pm .214$ .

From the ratio between the  $\text{K}_2\text{SO}_4$  and the  $\text{ThO}_2$  in the double sulphate,  $\text{ThO}_2 = 266.895$ .

In 1861 new determinations were published by Chydenius,† whose memoir is accessible to me only in an abstract‡ which gives results without details. Thoria is regarded as a monoxide,  $\text{ThO}$ , and the old equivalents ( $\text{O} = 8$ ) are used. The following values are assigned for the molecular weight of  $\text{ThO}$ , as found from analyses of several salts:

<i>From Sulphate.</i>		<i>From K. Th. Sulphate.</i>	
	66.33		67.02
	67.13		
	67.75		
	68.03		
<hr/>		<hr/>	
Mean, 67.252, $\pm .201$			
<i>From Acetate.</i>		<i>From Formate.</i>	<i>From Oxalate.</i>
67.31		68.06	65.87
66.59		67.89	65.95
67.27		68.94	65.75
67.06		<hr/>	65.13
68.40		Mean, 68.297, $\pm .219$	66.54
<hr/>			65.85
Mean, 67.326, $\pm .201$			<hr/>
			Mean, 65.85, $\pm .123$

\* Poggend. Annal., 16, 398. 1829. Lehrbuch, 3, 1224.

† Kemisk undersökning af Thorjord och Thorsalter. Helsingfors, 1861. An academic dissertation.

‡ Poggend. Annal., 119, 55. 1863.



We may fairly assume that these figures were calculated with  $O = 8$ ,  $C = 6$ , and  $S = 16$ . Correcting by the values for these elements which have been found in previous chapters,  $ThO_2$  becomes as follows:

From sulphate .....	$ThO_2 = 267.170, \pm .7950$
From acetate.....	" $= 267.488, \pm .7950$
From formate.....	" $= 271.239, \pm .8698$
From oxalate .....	" $= 261.478, \pm .4884$
<hr/>	
General mean.....	$ThO_2 = 265.103, \pm .3394$

The single result from the double potassium sulphate is included with the column from the ordinary sulphate, and the influence of the atomic weight of potassium is ignored.

Chydenius was soon followed by Marc Delafontaine, whose researches appeared in 1863.\* This chemist especially studied thorium sulphate; partly in its most hydrous form, partly as thrown down by boiling. In  $Th(SO_4)_2 \cdot 9H_2O$ , the following percentages of  $ThO_2$  were found:

45.08  
44.90  
45.06  
45.21  
45.06

Mean, 45.062,  $\pm .0332$

The lower hydrate,  $2Th(SO_4)_2 \cdot 9H_2O$ , was more thoroughly investigated. The thoria was estimated in two ways: First (A), by precipitation as oxalate and subsequent ignition; second (B), by direct calcination. These percentages of  $ThO_2$  were found:

52.83 }  
52.52 } A.  
52.72 }  
52.13 }  
52.47 }  
52.49 }  
52.53 }  
52.13 }  
52.13 } B.  
52.43 }  
52.60 }  
52.40 }  
52.96 }  
52.82 }

Mean, 52.511,  $\pm .047$

In three experiments with this lower hydrate the sulphuric acid was also estimated, being thrown down as barium sulphate after removal of the thoria:

\* Arch. Sci. Phys. et Nat. (2), 18, 343.

1.2425	gram.	gave .400	SO <sub>3</sub> .	(1.1656	gram.	BaSO <sub>4</sub> .)
1.138	"	.366	"	(1.0665	"	)
.734	"	.2306	"	(.6720	"	)

The figures in parentheses are reproduced by myself from Delafontaine's results, he having calculated his analyses with O = 100, S = 200, and Ba = 857. These data may be reduced to a common standard, so as to represent the quantity of 2Th(SO<sub>4</sub>)<sub>2</sub>·9H<sub>2</sub>O, equivalent to 100 parts of BaSO<sub>4</sub>. We then have the following results :

106.597
106.704
109.226
Mean, 107.509, ± .585

Delafontaine was soon followed by Hermann,\* who published a single analysis of the lower hydrated sulphate, as follows :

ThO <sub>2</sub> ..	.....	52.87
SO <sub>3</sub> .....	.....	32.11
H <sub>2</sub> O.....	.....	15.02
		100.00

Hence, from the ratio between SO<sub>3</sub> and ThO<sub>2</sub>, ThO<sub>2</sub> = 262.286. Probably the SO<sub>3</sub> percentage was lost upon calcination.

Both Hermann's results and those of Delafontaine are affected by one serious doubt, namely, as to the true composition of the lower hydrated sulphate. The latest and best evidence seems to establish the fact that it contains four molecules of water instead of four and a half,† a fact which tends to lower the resulting atomic weight of thorium considerably. In the final discussion of these data, therefore, the formula Th(SO<sub>4</sub>)<sub>2</sub>·4H<sub>2</sub>O will be adopted. As for Hermann's single analysis, his percentage of ThO<sub>2</sub>, 52.87, may be included in one series with Delafontaine's, giving a mean of 52.535, ± .0473.

The next determinations to consider are those of Cleve,‡ whose results, obtained from both the sulphate and the oxalate of thorium, agree admirably. The anhydrous sulphate, calcined, gave the subjoined percentages of thoria :

62.442
62.477
62.430
62.470
62.357
62.366
Mean, 62.423, ± .014

\* Journ. für Prakt. Chem., 93, 114.

† See Hillebrand, Bull. 90, U. S. Geol. Survey, p. 29.

‡ K. Svenska Vet. Akad. Handling., Bd. 2, No. 6, 1874.

The oxalate was subjected to a combustion analysis, whereby both thoria and carbonic acid could be estimated. From the direct percentages of these constituents no accurate value can be deduced, there having undoubtedly been moisture in the material studied. From the ratio between  $\text{CO}_2$  and  $\text{ThO}_2$ , however, good results are attainable. This ratio I put in a fourth column, making the thoria proportional to 100 parts of carbon dioxide:

<i>Oxalate.</i>	<i>ThO<sub>2</sub>.</i>	<i>CO<sub>2</sub>.</i>	<i>Ratio.</i>
1.7135 grm.	1.0189 grm.	.6736 grm.	151.262
1.3800 "	.8210 "	.5433 "	151.114
1.1850 "	.7030 "	.4650 "	151.183
1.0755 "	.6398 "	.4240 "	150.896
<hr/>			
Mean, 151.114, $\pm .053$			

In 1882, Nilson's determinations appeared.\* This chemist studied both the anhydrous sulphate, and the salt with nine molecules of water, using the usual calcination method, but guarding especially against the hygroscopic character of the dry  $\text{Th}(\text{SO}_4)_2$  and the calcined  $\text{ThO}_2$ . The hydrated sulphate gave results as follows:

<i>Th(SO<sub>4</sub>)<sub>2</sub>.9H<sub>2</sub>O.</i>	<i>ThO<sub>2</sub>.</i>	<i>Per cent. ThO<sub>2</sub>.</i>
2.0549	.9267	45.097
2.1323	.9615	45.092
3.0017	1.3532	45.081
2.7137	1.2235	45.086
2.6280	1.1849	45.088
1.9479	.8785	45.099
<hr/>		
Mean, 45.091, $\pm .0019$		
Delafontaine found, 45.062, $\pm .0332$		
<hr/>		
General mean, 45.090, $\pm .0019$		

The anhydrous sulphate gave data as follows:

<i>Th(SO<sub>4</sub>)<sub>2</sub>.</i>	<i>ThO<sub>2</sub>.</i>	<i>Per cent. ThO<sub>2</sub>.</i>
1.4467	.9013	62.300
1.6970	1.0572	62.298
2.0896	1.3017	62.294
1.5710	.9787	62.298
<hr/>		
Mean, 62.297, $\pm .0009$		

The last four determinations appear again in a paper published five years later by Krüss and Nilson,† who, however, give four more made

\* Ber. Deutsch. Chem. Gesell., 15, 2519. 1882.

† Ber. Deutsch. Chem. Gesell., 20, 1665. 1887.

upon material obtained from a different source. The new data are sub-joined :

$Th(SO_4)_2$ .	$ThO_2$ .	<i>Per cent. <math>ThO_2</math>.</i>
1.1630	.7245	62.296
.8607	.5362	62.298
1.5417	.9605	62.301
1.5217	.9479	62.292
		<hr/>
		Mean, 62.297, $\pm .0013$
		Nilson's series, 62.297, $\pm .0009$
		Cleve found, 62.423, $\pm .0140$
		<hr/>
		General mean, 62.298, $\pm .0007$

From Chydenius' work we have four values for the molecular weight of thoria, which, combined as usual, give a general mean of  $ThO_2 = 265.103, \pm .3394$ . We also have the following ratios :

- (1.)  $2BaSO_4 : ThO_2 :: 100 : 58.026, \pm .214$
- (2.)  $2BaSO_4 : Th(SO_4)_2 \cdot 4H_2O :: 100 : 107.509, \pm .585$
- (3.)  $4CO_2 : ThO_2 :: 100 : 151.114, \pm .053$
- (4.) Percentage of  $ThO_2$  in  $Th(SO_4)_2 \cdot 9H_2O$ , 45.090,  $\pm .0019$
- (5.) Percentage of  $ThO_2$  in  $Th(SO_4)_2 \cdot 4H_2O$ , 52.535,  $\pm .0473$
- (6.) Percentage of  $ThO_2$  in  $Th(SO_4)_2$ , 62.298,  $\pm .0007$

Reducing with the following data, seven values for the atomic weight of thoria are calculable :

O = 15.879, $\pm .0003$	C = 11.920, $\pm .0004$
S = 31.828, $\pm .0015$	Ba = 136.392, $\pm .0086$

The values for  $ThO_2$  are—

Chydenius' determinations.....	$ThO_2 = 265.103, \pm .3394$
From (1).....	" = 268.937, $\pm .9919$
From (2).....	" = 268.021, $\pm 2.7115$
From (3).....	" = 264.120, $\pm .0927$
From (4).....	" = 262.641, $\pm .0149$
From (5).....	" = 255.061, $\pm .3426$
From (6).....	" = 262.613, $\pm .0081$
<hr/>	
General mean.....	$ThO_2 = 262.626, \pm .0071$

Hence  $Th = 230.868, \pm .0071$ .

If O = 16,  $Th = 232.626$ .

## PHOSPHORUS.

The material from which we are to calculate the atomic weight of phosphorus is by no means abundant. Berzelius, in his *Lehrbuch*,\* adduces only his own experiments upon the precipitation of gold by phosphorus, and ignores all the earlier work relating to the composition of the phosphates. These experiments have been considered with reference to gold.

Pelouze,† in a single titration of phosphorus trichloride with a standard solution of silver, obtained a wholly erroneous result; and Jacquelin,‡ in his similar experiments, did even worse. Schrötter's criticism upon Jacquelin sufficiently disposes of the latter. §

Only the determinations made by Schrötter, Dumas, and Van der Plaats remain to be considered.

Schrötter|| burned pure amorphous phosphorus in dry oxygen, and weighed the pentoxide thus formed. One gramme of P yielded  $P_2O_5$  in the following proportions:

2.28909
2.28783
2.29300
2.28831
2.29040
2.28788
2.28848
2.28856
2.28959
2.28872

Mean, 2.289186,  $\pm .00033$

Dumas¶ prepared pure phosphorus trichloride by the action of dry chlorine upon red phosphorus. The portion used in his experiments boiled between  $76^\circ$  and  $78^\circ$ . This was titrated with a standard solution of silver in the usual manner. Dumas publishes weights, from which I calculate the figures given in the third column, representing the quantity of trichloride proportional to 100 parts of silver:

1.787	gram.	$PCl_3 = 4.208$	gram.	Ag.	42.4667
1.466	"	3.454	"	"	42.4435
2.056	"	4.844	"	"	42.4443
2.925	"	6.890	"	"	42.4528
3.220	"	7.582	"	"	42.4690

Mean, 42.4553,  $\pm .0036$

\* 5th ed., 1188.

† *Compt. Rend.*, 20, 1047.

‡ *Compt. Rend.*, 33, 693.

§ *Journ. für Prakt. Chem.*, 57, 315.

|| *Journ. für Prakt. Chem.*, 53, 435. 1851.

¶ *Ann. Chem. Pharm.*, 113, 29. 1860.

By Van der Plaats\* three methods of determination were adopted, and all weights were reduced to vacuum standards. First, silver was precipitated from a solution of the sulphate by means of phosphorus. The latter had been twice distilled in a current of nitrogen. The silver, before weighing, was heated to redness. The phosphorus equivalent to 100 parts of silver is given in the third column.

.9096 gm. P gave 15.8865 Ag.	5.7256
.5832        "        10.1622 "	5.7389
	<hr/>
Mean, 5.7322, $\pm$ .0045	

The second method consisted in the analysis of silver phosphate; but the process is not given. Van der Plaats states that it is difficult to be sure of the purity of this salt.

6.6300 gm. $\text{Ag}_3\text{PO}_4$ gave 5.1250 Ag.	77.300 per cent.
12.7170        "        9.8335 "	77.326 "
	<hr/>
Mean, 77.313, $\pm$ .0088	

In the third set of determinations, yellow phosphorus was oxidized by oxygen at reduced pressure, and the resulting  $\text{P}_2\text{O}_5$  was weighed.

10.8230 gm. P gave 24.7925 $\text{P}_2\text{O}_5$ .	Ratio, 2 29072
7.7624        "        17.7915 "	"    2.29201

As these figures fall within the range of Schrötter's, they may be averaged in with his series, the entire set of twelve determinations giving a mean of 2.28955,  $\pm$  .00032.

From the following ratios an equal number of values for P may now be computed:

- (1.)  $2\text{P} : \text{P}_2\text{O}_5 :: 1.0 : 2.28955, \pm .00032$
- (2.)  $3\text{Ag} : \text{PCl}_3 :: 100 : 42.4553, \pm .0036$
- (3.)  $5\text{Ag} : \text{P} :: 100 : 5.7322, \pm .0045$
- (4.)  $\text{Ag}_3\text{PO}_4 : 3\text{Ag} :: 100 : 77.313, \pm .0088$

Starting with  $\text{O} = 15.879, \pm .0003$ ,  $\text{Ag} = 107.108, \pm .0031$ , and  $\text{Cl} = 35.179, \pm .0048$ , we have—

From (1).....	P = 30.784, $\pm$ .0077
From (2).....	" = 30.882, $\pm$ .0189
From (3).....	" = 30.698, $\pm$ .0241
From (4).....	" = 30.774, $\pm$ .0382
	<hr/>
General mean.....	P = 30.789, $\pm$ .0067

If  $\text{O} = 16$ ,  $\text{P} = 31.024$ .

The highest of these figures is that from ratio number two, representing the work of Dumas. This is possibly due to the presence of oxy-chloride, in traces, in the trichloride taken. Such an impurity, if present, would tend to raise the apparent atomic weight of phosphorus.

## VANADIUM.

Roscoe's determination of the atomic weight of vanadium was the first to have any scientific value. The results obtained by Berzelius\* and by Czudnowicz† were unquestionably too high, the error being probably due to the presence of phosphoric acid in the vanadic acid employed. This particular impurity, as Roscoe has shown, prevents the complete reduction of  $V_2O_5$  to  $V_2O_3$  by means of hydrogen. All vanadium ores contain small quantities of phosphorus, which can only be detected with ammonium molybdate—a reaction unknown in Berzelius' time. Furthermore, the complete purification of vanadic acid from all traces of phosphoric acid is a matter of great difficulty, and probably never was accomplished until Roscoe undertook his researches.

In his determination of the atomic weight, Roscoe‡ studied two compounds of vanadium, namely, the pentoxide,  $V_2O_5$ , and the oxychloride,  $VOCl_3$ . The pentoxide, absolutely pure, was reduced to  $V_2O_3$  by heating in hydrogen, with the following results:

7.7397	gram.	$V_2O_5$	gave	6.3827	gram.	$V_2O_3$ .	17.533	per cent. of loss.
6.5819		"		5.4296		"	17.507	"
5.1895		"		4.2819		"	17.489	"
5.0450		"		4.1614		"	17.515	"
5.4296	gram.	$V_2O_3$ ,	reoxidized,	gave	6.5814	gram.	$V_2O_5$ .	17.501

per cent. difference.

Mean, 17.509,  $\pm$  .005

Hence  $V = 50.993, \pm .0219$ .

Upon the oxychloride,  $VOCl_3$ , two series of experiments were made—one volumetric, the other gravimetric. In the volumetric series the compound was titrated with solutions containing known weights of silver, which had been purified according to the methods recommended by Stas. Roscoe publishes his weighings, and gives percentages deduced from them; his figures, reduced to a common standard, make the quantities of  $VOCl_3$  given in the third column proportional to 100 parts of silver. He was assisted by two analysts:

*Analyst A.*

2.4322	gram.	$VOCl_3$	=	4.5525	gram.	Ag.	53.425
4.6840		"		8.7505		"	53.528
4.2188		"		7.8807		"	53.533
3.9490		"		7.3799		"	53.510
.9243		"		1.7267		"	53.530
1.4330		"		2.6769		"	53.532

\* Poggend. Annal., 22, 14. 1831.

† Poggend. Annal., 120, 17. 1863.

‡ Journ. Chem. Soc., 6, pp. 320 and 344. 1868.

*Analyst B.*

2.8530	gm.	$\text{VOCl}_3$	=	5.2853	gm.	Ag.	53.980
2.1252		"		3.9535		"	53.755
1.4248		"		2.6642		"	53.479
							<hr/>
							Mean, 53.586, $\pm .039$

The gravimetric series, of course, fixes the ratio between  $\text{VOCl}_3$  and  $\text{AgCl}$ . If we put the latter at 100 parts, the proportion of  $\text{VOCl}_3$  is as given in the third column:

*Analyst A.*

1.8521	gm.	$\text{VOCl}_3$	gave	4.5932	gm.	$\text{AgCl}$ .	40.323
.7013		"		1.7303		"	40.531
.7486		"		1.8467		"	40.537
1.4408		"		3.5719		"	40.337
.9453		"		2.3399		"	40.399
1.6183		"		4.0282		"	40.174

*Analyst B.*

2.1936	gm.	$\text{VOCl}_3$	gave	5.4039	gm.	$\text{AgCl}$ .	40.391
2.5054		"		6.2118		"	40.333
							<hr/>
							Mean, 40.378, $\pm .028$

These two series give us two values for the molecular weight of  $\text{VOCl}_3$ :

From volumetric series.....	$\text{VOCl}_3 = 172.185, \pm .1254$
From gravimetric series.....	" = $172.358, \pm .1196$
<hr/>	
General mean.....	$\text{VOCl}_3 = 172.277, \pm .0866$

Hence  $V = 50.881, \pm .0877$ .

Combining the two values for  $V$ , we have:

From $\text{VOCl}_3$ .....	$V = 50.881, \pm .0877$
From $\text{V}_2\text{O}_5$ .....	" = $50.993, \pm .0219$
<hr/>	
General mean.....	$V = 50.986, \pm .0212$

If  $O = 16$ ,  $V = 51.376$ . These values are calculated with  $O = 15.879, \pm .0003$ ;  $\text{Cl} = 35.179, \pm .0048$ ;  $\text{Ag} = 107.108, \pm .0031$ , and  $\text{AgCl} = 142.287, \pm .0037$ .



## ARSENIC.

For the determination of the atomic weight of arsenic three compounds have been studied—the chloride, the trioxide, and sodium pyroarsenate. The bromide may also be considered, since it was analyzed by Wallace in order to establish the atomic weight of bromine. His series, in the light of more recent knowledge, may properly be inverted, and applied to the determination of arsenic.

In 1826 Berzelius\* heated arsenic trioxide with sulphur in such a way that only  $\text{SO}_2$  could escape. 2.203 grammes of  $\text{As}_2\text{O}_3$ , thus treated, gave a loss of 1.069 of  $\text{SO}_2$ . Hence  $\text{As} = 74.460$ .

In 1845 Pelouze† applied his method of titration with known quantities of pure silver to the analysis of the trichloride of arsenic,  $\text{AsCl}_3$ . Using the old Berzelian atomic weights, and putting  $\text{Ag} = 1349.01$  and  $\text{Cl} = 443.2$ , he found in three experiments for As the values 937.9, 937.1, and 937.4. Hence 100 parts of silver balance the following quantities of  $\text{AsCl}_3$ :

56.029
56.009
56.016
<hr/>
Mean, 56.018, $\pm .004$

Later, the same method was employed by Dumas‡ whose weighings, reduced to the foregoing standard, give the following results:

4.298 grm.	$\text{AsCl}_3 = 7.673$ grm.	Ag.	Ratio, 56.015
5.535	“	9.880	“ 56.022
7.660	“	13.686	“ 55.970
4.680	“	8.358	“ 55.993
<hr/>			
Mean, 56.000, $\pm .008$			

The two series of Pelouze and Dumas, combined, give a general mean of 56.014,  $\pm .0035$ , as the amount of  $\text{AsCl}_3$  equivalent to 100 parts of silver. Hence  $\text{As} = 74.450$ ,  $\pm .019$ , a value closely agreeing with that deduced from the single experiment of Berzelius.

The same process of titration with silver was applied by Wallace§ to the analysis of arsenic tribromide,  $\text{AsBr}_3$ . This compound was repeatedly distilled to ensure purity, and was well crystallized. His weighings show that the quantities of bromide given in the third column are proportional to 100 parts of silver:

8.3246 grm.	$\text{AsBr}_3 = 8.58$ grm.	Ag.	97.023
4.4368	“	4.573	“ 97.022
5.098	“	5.257	“ 96.970
<hr/>			
Mean, 97.005, $\pm .012$			

\* Poggend. Annalen, 8, 1.

† Compt. Rend., 20, 1047.

‡ Ann. Chim. Phys. (3), 55, 174. 1859.

§ Phil. Mag. (4), 18, 270.

Hence  $\text{As} = 73.668, \pm .0436$ . Why this value should be so much lower than that from the chloride is unexplained.

The volumetric work done by Kessler,\* for the purpose of establishing the atomic weights of chromium and of arsenic, is described in the chromium chapter. In that investigation the amount of potassium dichromate required to oxidize 100 parts of  $\text{As}_2\text{O}_3$  to  $\text{As}_2\text{O}_5$  was determined and compared with the quantity of potassium chlorate necessary to produce the same effect. From the molecular weight of  $\text{KClO}_3$ , that of  $\text{K}_2\text{Cr}_2\text{O}_7$  was then calculable.

From the same figures, the molecular weights of  $\text{KClO}_3$  and of  $\text{K}_2\text{Cr}_2\text{O}_7$  being both known, that of  $\text{As}_2\text{O}_3$  may be easily determined. The quantities of the other compounds proportional to 100 parts of  $\text{As}_2\text{O}_3$  are as follows :

$\text{K}_2\text{Cr}_2\text{O}_7$ .	$\text{KClO}_3$ .
98.95	41.156
98.94	41.116
99.17	41.200
98.98	41.255
99.08	41.201
99.15	41.086
<hr/>	41.199
Mean, 99.045, $\pm .028$	41.224
	41.161
	41.193
	41.149
	41.126
	<hr/>
	Mean, 41.172, $\pm .009$

Another series with the dichromate gave the following figures :

99.08
99.06
99.10
98.97
98.97
<hr/>
Mean, 99.036, $\pm .019$
Previous series, 99.045, $\pm .028$
<hr/>
General mean, 99.039, $\pm .016$

Other defective series are given to illustrate the partial oxidation of the  $\text{As}_2\text{O}_3$  by the action of the air. From Kessler's data we get two values for the molecular weight of  $\text{As}_2\text{O}_3$ , thus :

From $\text{KClO}_3$ series.....	$\text{As}_2\text{O}_3 = 196.951, \pm .0445$
From $\text{K}_2\text{Cr}_2\text{O}_7$ series.....	" $= 196.726, \pm .0562$
<hr/>	
General mean.....	$\text{As}_2\text{O}_3 = 196.851, \pm .0349$

And  $\text{As} = 74.607, \pm .0175$ .

\* Poggend Annal., 95, 204. 1855. Also 113, 134. 1861.

The determinations made by Hibbs\* are based upon an altogether different process from any of the preceding measurements. Sodium pyroarsenate was heated in gaseous hydrochloric acid, yielding sodium chloride. The latter was perfectly white, completely soluble in water, unfused, and absolutely free from arsenic. The vacuum weights are subjoined, with a column giving the percentage of chloride obtained from the pyroarsenate.

$Na_4As_2O_7$ .	$NaCl$ .	Percentage.
.02177	.01439	66.100
.04713	.03115	66.094
.05795	.03830	66.091
.40801	.26981	66.128
.50466	.33345	66.092
.77538	.51249	66.095
.82897	.54791	66.095
1.19124	.78731	66.092
1.67545	1.10732	66.091
3.22637	2.13267	66.101

Mean, 66.098,  $\pm$  .0030

Hence As = 74.340,  $\pm$  .0235.

In the calculation of the foregoing values for arsenic, the subjoined atomic weights have been assumed :

O = 15.879, $\pm$ .0003	K = 38.817, $\pm$ .0051
Ag = 107.108, $\pm$ .0031	Na = 22.881, $\pm$ .0046
Cl = 35.179, $\pm$ .0048	S = 31.828, $\pm$ .0015
Br = 79.344, $\pm$ .0062	Cr = 51.742, $\pm$ .0034

To the single determination by Berzelius we may arbitrarily assign a weight equal to that of the result from Wallace's bromide series. The general combination is then as follows :

From Berzelius' experiment . . . . .	As = 74.460, $\pm$ .0436
From $AsCl_3$ . . . . .	" = 74.450, $\pm$ .0190
From $AsBr_3$ . . . . .	" = 73.668, $\pm$ .0436
From $As_2O_3$ (Kessler) . . . . .	" = 74.607, $\pm$ .0175
From $Na_4As_2O_7$ . . . . .	" = 74.340, $\pm$ .0235
General mean . . . . .	As = 74.440, $\pm$ .0106

If O = 16, As = 75.007.

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\* Doctoral thesis, University of Pennsylvania, 1896. Work done under the direction of Professor E. F. Smith. In the fifth experiment the weight of NaCl is printed .33045. This is evidently a misprint, which I have corrected by comparison with the other data. The rejection of this experiment would not affect the final result appreciably.

## ANTIMONY.

After some earlier, unsatisfactory determinations, Berzelius,\* in 1826, published his final estimation of the atomic weight of antimony. He oxidized the metal by means of nitric acid, and found that 100 parts of antimony gave 124.8 of  $\text{Sb}_2\text{O}_3$ . Hence, if  $\text{O} = 16$ ,  $\text{Sb} = 129.03$ . The value 129 remained in general acceptance until 1855, when Kessler, † by special volumetric methods, showed that it was certainly much too high. Kessler's results will be considered more fully further along, in connection with a later paper; for present purposes a brief statement of his earlier conclusions will suffice. Antimony and various compounds of antimony were oxidized partly by potassium dichromate and partly by potassium chlorate, and from the amounts of oxidizing agent required the atomic weight in question was deduced:

By oxidation of $\text{Sb}_2\text{O}_3$ from 100 parts of Sb. . . . .	$\text{Sb} = 123.84$
By oxidation of Sb with $\text{K}_2\text{Cr}_2\text{O}_7$ . . . . .	" = 123.61
By oxidation of Sb with $\text{KClO}_3 + \text{K}_2\text{Cr}_2\text{O}_7$ . . . . .	" = 123.72
By oxidation of $\text{Sb}_2\text{O}_3$ with $\text{KClO}_3 + \text{K}_2\text{Cr}_2\text{O}_7$ . . . . .	" = 123.80
By oxidation of $\text{Sb}_2\text{S}_3$ with $\text{K}_2\text{Cr}_2\text{O}_7$ . . . . .	" = 123.58
By oxidation of tartar emetic . . . . .	" = 119.80

The figures given are those calculated by Kessler himself. A recalculation with our newer atomic weights for O, K, Cl, Cr, S, and C would yield lower values. It will be seen that five of the estimates agree closely, while one diverges widely from the others. It will be shown hereafter that the concordant values are all vitiated by constant errors, and that the exceptional figure is after all the best.

Shortly after the appearance of Kessler's first paper, Schneider ‡ published some results obtained by the reduction of antimony sulphide in hydrogen. The material chosen was a very pure stibnite from Arnsberg, of which the gangue was only quartz. This was corrected for, and corrections were also applied for traces of undecomposed sulphide carried off mechanically by the gas stream, and for traces of sulphur retained by the reduced antimony. The latter sulphur was estimated as barium sulphate. From 3.2 to 10.6 grammes of material were taken in each experiment. The final corrected percentages of S in  $\text{Sb}_2\text{S}_3$  were as follows:

28.559
28.557
28.501
28.554
28.532

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\* Poggend. Annalen, 8, 1.

† Poggend. Annalen, 95, 215.

‡ Poggend. Annalen, 98, 293. 1856. Preliminary note in Bd. 97.

28.485

28.492

28.481

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 Mean, 28.520,  $\pm .008$ 

Hence, if  $S = 32$ ,  $Sb = 120.3$ .

Immediately after the appearance of Schneider's memoir, Rose\* published the result of a single analysis of antimony trichloride, previously made under his supervision by Weber. This analysis, if  $Cl = 35.5$ , makes  $Sb = 120.7$ , a value of no great weight, but in a measure confirmatory of that obtained by Schneider.

The next research upon the atomic weight of antimony was that of Dexter,† published in 1857. This chemist, having tried to determine the amount of gold precipitable by a known weight of antimony, and having obtained discordant results, finally resorted to the original method of Berzelius. Antimony, purified with extreme care, was oxidized by nitric acid, and the gain in weight was determined. From 1.5 to 3.3 grammes of metal were used in each experiment. The reduction of the weights to a vacuum standard was neglected as being superfluous. From the data obtained, we get the following percentages of  $Sb$  in  $Sb_2O_3$ :

79.268

79.272

79.255

79.266

79.253

79.271

79.264

79.260

79.286

79.274

79.232

79.395

79.379

---

 Mean, 79.283,  $\pm .009$ 

Hence, if  $O = 16$ ,  $Sb = 122.46$ .

The determinations of Dumas‡ were published in 1859. This chemist sought to fix the ratio between silver and antimonious chloride, and obtained results for the atomic weight of antimony quite near to those of Dexter. The  $SbCl_3$  was prepared by the action of dry chlorine upon pure antimony; it was distilled several times over antimony powder, and it seemed to be perfectly pure. Known weights of this preparation were added to solutions of tartaric acid in water, and the silver chloride was precipitated without previous removal of the antimony. Here, as

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\* Poggend. Annalen, 98, 455. 1856.

† Poggend. Annalen, 100, 363. 1857.

‡ Ann. Chim. Phys. (3), 55, 175.

Cooke has since shown, is a possible source of error, for under such circumstances the crystalline argento-antimonious tartrate may also be thrown down and contaminate the chloride of silver. But be that as it may, Dumas' weighings, reduced to a common standard, give as proportional to 100 parts of silver, the quantities of  $\text{SbCl}_3$  which are stated in the third of the subjoined columns:

1.876	gram.	$\text{SbCl}_3 = 2.660$	gram.	Ag.	70.526
4.336	"	6.148	"	"	70.527
5.065	"	7.175	"	"	70.592
3.475	"	4.930	"	"	70.487
3.767	"	5.350	"	"	70.411
5.910	"	8.393	"	"	70.416
4.828	"	6.836	"	"	70.626

Mean, 70.512,  $\pm .021$

Hence, if  $\text{Ag} = 108$ , and  $\text{Cl} = 35.5$ ,  $\text{Sb} = 122$ .

In 1861 Kessler's second paper\* relative to the atomic weight of antimony appeared. Kessler's methods were somewhat complicated, and for full details the original memoirs must be consulted. A standard solution of potassium dichromate was prepared, containing 6.1466 grammes to the litre. With this, solutions containing known quantities of antimony or of antimony compounds were titrated, the end reaction being adjusted with a standard solution of ferrous chloride. In some cases the titration was preceded by the addition of a definite weight of potassium chlorate, insufficient for complete oxidation; the dichromate then served to finish the reaction. The object in view was to determine the amount of oxidizing agent, and therefore of oxygen, necessary for the conversion of known quantities of antimonious into antimonie compounds.

In the later paper Kessler refers to his earlier work, and shows that the values then found for antimony were all too high, except in the case of the series made with tartar emetic. That series he merely states, and subsequently ignores, evidently believing it to be unworthy of further consideration. For the remaining series he points out the sources of error. These need not be rediscussed here, as the discussion would have no value for present purposes; suffice it to say that in the series representing the oxidation of  $\text{Sb}_2\text{O}_3$  with dichromate and chlorate, the material used was found to be impure. Upon estimating the impurity and correcting for it, the earlier value of  $\text{Sb} = 123.80$  becomes  $\text{Sb} = 122.36$ , according to Kessler's calculations.

In the paper now under consideration four series of results are given. The first represents experiments made upon a pure antimony trioxide which had been sublimed, and which consisted of shining colorless needles. This was dissolved, together with some potassium chlorate, in

\* Poggend. Annalen, 113, 145. 1861.

hydrochloric acid, and titrated with dichromate solution. Six experiments were made, but Kessler rejects the first and second as untrustworthy. The data for the others are as follows:

$Sb_2O_3$ .	$KClO_3$ .	$K_2Cr_2O_7$ sol. in cc.
1.7888 gm.	.4527 gm.	19.2 cc.
1.6523 "	.4506 "	3.9 "
3.2998 "	.8806 "	16.5 "
1.3438 "	.3492 "	10.2 "

From these figures Kessler deduces  $Sb = 122.16$ .

These data, reduced to a common standard, give the following quantities of oxygen needed to oxidize 100 parts of  $Sb_2O_3$  to  $Sb_2O_5$ . Each cubic centimetre of the  $K_2Cr_2O_7$  solution corresponds to one milligramme of O:

10.985
10.939
10.951
10.936

Mean, 10.953,  $\pm .0075$

In the second series of experiments pure antimony was dissolved in hydrochloric acid with the aid of an unweighed quantity of potassium chlorate. The solution, containing both antimonious and antimonic compounds, was then reduced entirely to the antimonious condition by means of stannous chloride. The excess of the latter was corrected with a strong hydrochloric acid solution of mercuric chloride, then, after diluting and filtering, a weighed quantity of potassium chlorate was added, and the titration with dichromate was performed as usual. Calculated as above, the percentages of oxygen given in the last column correspond to 100 parts of antimony:

$Sb$ .	$KClO_3$ .	$K_2Cr_2O_7$ sol. cc.	Per cent. O.
1.636 gm.	0.5000 gm.	18.3	13.088
3.0825 "	0.9500 "	30.2	13.050
4.5652 "	1.4106 "	45.5	13.098

Mean, 13.079,  $\pm .0096$

This series gave Kessler  $Sb = 122.34$ .

The third and fourth series of experiments were made with pure antimony trichloride,  $SbCl_3$ , prepared by the action of mercuric chloride upon metallic antimony. This preparation, in the third series, was dissolved in hydrochloric acid, and titrated. In one experiment solid  $K_2Cr_2O_7$  in weighed amount was added before titration; in the other two estimations  $KClO_3$  was taken as usual. The third column gives the percentages of oxygen corresponding to 100 parts of  $SbCl_3$ .

					<i>Per cent. O.</i>
1.8576	gram. $\text{SbCl}_3$ needed	.5967	gram. $\text{K}_2\text{Cr}_2\text{O}_7$ and	33.4 cc. sol.	7.0338
1.9118	"	.3019	" $\text{KClO}_3$	" 16.2 "	7.0321
4.1235	"	.6801	" $\text{KClO}_3$	" 23.2 "	<u>7.0222</u>
Mean,					7.0294, $\pm .0024$

The fourth set of experiments was gravimetric. The solution of  $\text{SbCl}_3$ , mixed with tartaric acid, was first precipitated by hydrogen sulphide, in order to remove the antimony. The excess of  $\text{H}_2\text{S}$  was corrected by copper sulphate, and then the chlorine was estimated as silver chloride in the ordinary manner. 100 parts of  $\text{AgCl}$  correspond to the amounts of  $\text{SbCl}_3$  given in the third column.

1.8662	gram. $\text{SbCl}_3$ gave	3.483	gram. $\text{AgCl}$ .	53.580
1.6832	"	3.141	"	53.588
2.7437	"	5.1115	"	53.677
2.6798	"	5.0025	"	53.569
5.047	"	9.411	"	53.629
3.8975	"	7.2585	"	<u>53.696</u>
Mean,				53.623, $\pm .015$

The volumetric series with  $\text{SbCl}_3$  gave Kessler values for Sb ranging from 121.16 to 121.47. The gravimetric series, on the other hand, yielded results from  $\text{Sb} = 124.12$  to 124.67. This discrepancy Kessler rightly attributes to the presence of oxygen in the chloride; and, ingeniously correcting for this error, he deduces from both sets combined the value of  $\text{Sb} = 122.37$ .

The several mean results for antimony agree so fairly with each other, and with the estimates obtained by Dexter and Dumas, that we cannot wonder that Kessler felt satisfied of their general correctness, and of the inaccuracy of the figures published by Schneider. Still, the old series of data obtained by the titration of tartar emetic with dichromate contained no evident errors, and was not accounted for. This series,\* if we reduce all of Kessler's figures to a single common standard, gives a ratio between  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{C}_4\text{H}_4\text{KSbO}_7 \cdot \frac{1}{2}\text{H}_2\text{O}$ . 100 parts of the former will oxidize of the latter:

336.64
338.01
336.83
337.93
338.59
<u>335.79</u>
Mean, 337.30, $\pm .29$

From this, if  $\text{K}_2\text{Cr}_2\text{O}_7 = 292.271$ ,  $\text{Sb} = 118.024$ .

The newer atomic weights found in other chapters of this work will

\* Poggend. Annalen, 95, 217.



be applied to the discussion of all these series further along. It may, however, be properly noted at this point that the probable errors assigned to the percentages of oxygen in three of Kessler's series are too low. These percentages are calculated from the quantities of  $\text{KClO}_3$  involved in the several reactions, and their probable errors should be increased with reference to the probable error of the molecular weight of that salt. The necessary calculations would be more laborious than the importance of the figures would warrant, and accordingly, in computing the final general mean for antimony, Kessler's figures will receive somewhat higher weight than they are legitimately entitled to.

Naturally, the concordant results of Dexter, Kessler, and Dumas led to the general acceptance of the value of 122 for antimony as against the lower figure, 120, of Schneider. Still, in 1871, Unger\* published the results of a single analysis of Schlippe's salt,  $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$ . This analysis gave  $\text{Sb} = 119.76$ , if  $\text{S} = 32$  and  $\text{Na} = 23$ , but no great weight could be attached to the determination. It served, nevertheless, to show that the controversy over the atomic weight of antimony was not finally settled.

More than ten years after the appearance of Kessler's second paper the subject of the atomic weight of antimony was again taken up, this time by Professor Cooke. His results appeared in the autumn of 1877† and were conclusive in favor of the lower value, approximately 120. For full details the original memoir must be consulted: only a few of the leading points can be cited here.

Schneider analyzed a sulphide of antimony which was already formed. Cooke, reversing the method, effected the synthesis of this compound. Known weights of pure antimony were dissolved in hydrochloric acid containing a little nitric acid. In this solution weighed balls of antimony were boiled until the liquid became colorless; subsequently the weight of metal lost by the balls was ascertained. To the solution, which now contained only antimonious compounds, tartaric acid was added, and then, with a supersaturated aqueous sulphhydric acid, antimony trisulphide was precipitated. The precipitate was collected by an ingenious process of reverse filtration, converted into the black modification by drying at  $210^\circ$ , and weighed. After weighing, the  $\text{Sb}_2\text{S}_3$  was dissolved in hydrochloric acid, leaving a carbonaceous residue unacted upon. This was carefully estimated and corrected for. About two grammes of antimony were taken in each experiment and thirteen syntheses were performed. In two of these, however, the antimony trisulphide was weighed only in the red modification, and the results were uncorrected by conversion into the black variety and estimation of the carbonaceous residue. In fact, every such conversion and correction was preceded by a weighing of the red modification of the  $\text{Sb}_2\text{S}_3$ . The mean result of these weighings, if  $\text{S} = 32$ , gave  $\text{Sb} = 119.994$ . The mean result of the cor-

\* Archiv. der Pharmacie, 197, 194. Quoted by Cooke.

† Proc. Amer. Acad., 5, 13.

rected syntheses gave  $\text{Sb} = 120.295$ . In these eleven experiments the following percentages of S in  $\text{Sb}_2\text{S}_3$  were established :

28.57
28.60
28.57
28.43
28.42
28.53
28.50
28.49
28.58
28.50
28.51

Mean, 28.5182,  $\pm .0120$

These results, confirmatory of the work of Schneider, were presented to the American Academy in 1876. Still, before publication, Cooke thought it best to repeat the work of Dumas, in order to detect the cause of the old discrepancy between the values  $\text{Sb} = 120$  and  $\text{Sb} = 122$ . Accordingly, various samples of antimony trichloride were taken, and purified by repeated distillations. The final distillate was further subjected to several recrystallizations from the fused state; or, in one case, from a saturated solution in a bisulphide of carbon. The portions analyzed were dissolved in concentrated aqueous tartaric acid, and precipitated by silver nitrate, many precautions being observed. The silver chloride was collected by reverse filtration, and dried at temperatures from  $110^\circ$  to  $120^\circ$ . In one experiment the antimony was first removed by  $\text{H}_2\text{S}$ . Seventeen experiments were made, giving, if  $\text{Ag} = 108$  and  $\text{Cl} = 35.5$ , a mean value of  $\text{Sb} = 121.94$ . If we reduce to a common standard, Cooke's analyses give, as proportional to 100 parts of  $\text{AgCl}$ , the quantities of  $\text{SbCl}_3$  stated in the third column :

1.5974	gram, $\text{SbCl}_3$ gave	3.0124	gram, $\text{AgCl}$ .	53.028
1.2533	"	2.3620	"	53.061
.8876	"	1.6754	"	52.978
.8336	"	1.5674	"	53.184
.5326	"	1.0021	"	53.148
.7270	"	1.3691	"	53.101
1.2679	"	2.3883	"	53.088
1.9422	"	3.6646	"	52.999
1.7702	"	3.3384	"	53.025
2.5030	"	4.7184	"	53.048
2.1450	"	4.0410	"	53.081
1.7697	"	3.3281	"	53.175
2.3435	"	4.4157	"	53.072
1.3686	"	2.5813	"	53.020
1.8638	"	3.5146	"	53.030
2.0300	"	3.8282	"	53.028
2.4450	"	4.6086	"	53.053

Mean, 53.066,  $\pm .0096$

This mean may be combined with that of Kessler's series, as follows :

Kessler.....	53.623, $\pm .015$
Cooke.....	53.066, $\pm .0096$
General mean .....	<u>53.2311, <math>\pm .008</math></u>

The results thus obtained with  $\text{SbCl}_3$  confirmed Dumas' determination of the atomic weight of antimony as remarkably as the syntheses of  $\text{Sb}_2\text{S}_3$  had sustained the work of Schneider. Evidently, in one or the other series a constant error must be hidden, and much time was spent by Cooke in searching for it. It was eventually found that the chloride of antimony invariably contained traces of oxychloride, an impurity which tended to increase the apparent atomic weight of the metal under consideration. It was also found, in the course of the investigation, that hydrochloric acid solutions of antimonious compounds oxidize in the air during boiling as rapidly as ferrous compounds, a fact which explains the high values for antimony found by Kessler.

In order to render "assurance doubly sure," Professor Cooke also undertook the analysis of the bromide and the iodide of antimony. The bromide,  $\text{SbBr}_3$ , was prepared by adding the finely powdered metal to a solution of bromine in carbon disulphide. It was purified by repeated distillation over pulverized antimony, and by several recrystallizations from bisulphide of carbon. The bromine determinations resemble those of chlorine, and gave, if  $\text{Ag} = 108$  and  $\text{Br} = 80$ , a mean value for antimony of  $\text{Sb} = 120$ . Reduced to a common standard, the fifteen analyses give the subjoined quantities of  $\text{SbBr}_3$  proportional to 100 parts of silver bromide :

1.8621	gram. $\text{SbBr}_3$ gave	2.9216	gram. $\text{AgBr}$ .	63.736
.9856	"	1.5422	"	63.909
1.8650	"	2.9268	"	63.721
1.5330	"	2.4030	"	63.795
1.3689	"	2.1445	"	63.833
1.2124	"	1.8991	"	63.841
.9417	"	1.4749	"	63.848
2.5404	"	3.9755	"	63.901
1.5269	"	2.3905	"	63.874
1.8604	"	2.9180	"	63.756
1.7298	"	2.7083	"	63.870
3.2838	"	5.1398	"	63.890
2.3589	"	3.6959	"	63.825
1.3323	"	2.0863	"	63.859
2.6974	"	4.2285	"	63.791

Mean, 63.830,  $\pm .008$

The iodide of antimony was prepared like the bromide, and analyzed in the same way. At first, discordant results were obtained, due to the presence of oxyiodide in the iodide studied. The impurity, however,

was removed by subliming the iodide in an atmosphere of dry carbon dioxide. With this purer material, seven estimations of iodine were made, giving, if  $\text{Ag} = 108$  and  $\text{I} = 127$ , a value for antimony of  $\text{Sb} = 120$ . Reduced to a uniform standard, Cooke's weighings give the following quantities of  $\text{SbI}_3$  proportional to 100 parts of silver iodide:

1.1877	gram, $\text{SbI}_3$	gave 1.6727	gram, $\text{AgI}$ .	71.005
.4610	"	.6497	"	70.956
3.2527	"	4.5716	"	71.150
1.8068	"	2.5389	"	71.165
1.5970	"	2.2456	"	71.117
2.3201	"	3.2645	"	71.071
.3496	"	.4927	"	70.956

Mean, 71.060,  $\pm .023$

Although Cooke's work was practically conclusive, as between the rival values for antimony, his results were severely criticised by Kessler,\* who evidently had read Cooke's paper in a very careless way. On the other hand, Schneider published in Poggendorff's *Annalen* a friendly review of the new determinations, which so well vindicated his own accuracy. In reply to Kessler, Cooke undertook still another series of experiments with antimony bromide,† and obtained absolute confirmation of his previous results. To a solution of antimony bromide was added a solution containing a known weight of silver not quite sufficient to precipitate all the bromine. The excess of the latter was estimated by titration with a normal silver solution. Five analyses gave values for antimony ranging from 119.98 to 120.02, when  $\text{Ag} = 108$  and  $\text{Br} = 80$ . Reduced to a common standard, the weights obtained gave the amounts of  $\text{SbBr}$  stated in the third column as proportional to 100 parts of silver:

2.5032	gram, $\text{SbBr}_3$	= 2.2528	gram, $\text{Ag}$ .	111.115
2.0567	"	1.8509	"	111.119
2.6512	"	2.3860	"	111.115
3.3053	"	2.9749	"	111.106
2.7495	"	2.4745	"	111.113

Mean, 111.114,  $\pm .0014$

Schneider,‡ also, in order to more fully answer Kessler's objections, repeated his work upon the Arnsberg stibnite. This he reduced in hydrogen as before, correcting scrupulously for impurities. The following percentages of sulphur were found:

28.546
28.534
28.542

Mean, 28.541,  $\pm .0024$

\* *Berichte d. Deutsch. Chem. Gesell.*, 12, 1044. 1879.

† *Amer. Journ. Sci. and Arts*, May, 1880. *Berichte*, 13, 951.

‡ *Journ. für Prakt. Chem.* (2), 22, 131.

These figures confirm his old results, and may be fairly combined with them and with the percentages found by Cooke, as follows :

Schneider, early series.....	28.520, $\pm .008$
Schneider, late series.....	28.541, $\pm .0024$
Cooke .....	28.5182, $\pm .0120$
<hr/>	
General mean.....	28.5385, $\pm .0023$

In 1881 Pfeifer\* determined electrolytically the direct ratios between silver and antimony, and copper and antimony. With copper the following data were obtained :

$Cu_3 : Sb_2 :: 100 : x.$		
1.412 grm. Sb = 1.1008 Cu.		128.270
1.902     "     1.4832     "		128.236
3.367     "     2.6249     "		128.272
		<hr/>
Mean,		128.259, $\pm .0077$

If Cu = 63.6, Sb = 122.36.

With silver he found—

$Ag_3 : Sb :: 100 : x.$		
5.925 grm. Sb = 15.774 Ag.		37.562
6.429     "     17.109     "		37.577
10.116     "     26.972     "		37.506
4.865     "     13.014     "		37.383
4.390     "     11.697     "		37.531
9.587     "     25.611     "		37.433
4.525     "     12.097     "		37.406
		<hr/>
Mean,		37.485, $\pm .0198$

If Ag = 108, Sb = 121.45.

The latter ratio was also determined by Popper,† several years afterwards. The two metals were precipitated simultaneously by the same current; and in some experiments two portions of antimony were thrown down against one of silver. These are indicated in the subjoined table by suitable bracketing, and the ratio is given in the third column :

<i>Sb.</i>	<i>Ag.</i>	<i>Ratio.</i>
1.4856 }	3.9655	37.463
1.4788 }		37.292
2.0120 }	5.3649	37.503
2.0074 }		37.417
3.8882 }	10.3740	37.480
3.8903 }		37.500
4.1893 }	11.1847	37.455
4.1885 }		37.447

\* Ann. Chem. Pharm., 209, 161.

† Ann. Chem., 233, 153.

4.2710 }	11.3868	37.507
4.2752 }		37.545
5.6860 }	15.1786	37.460
5.6901 }		37.487
4.4117	11.8014	37.383
4.9999	13.3965	37.322
5.2409	14.0679	37.250

Mean, 37.434,  $\pm .0149$

Pfeifer found, 37.485,  $\pm .0198$

General mean, 37.452,  $\pm .0119$

If  $\text{Ag} = 108$ , Popper's figures give in mean  $\text{Sb} = 121.3$ .

I am inclined to attach slight importance to these electrolytic data, for the reasons that it would be very difficult to ensure the absolute purity and freedom from occlusions of the antimony as weighed, or to guarantee that no secondary reactions had modified the ratios.

The work done by Bongartz\* in 1883 was quite different from any of the determinations which had preceded it. Carefully purified antimony was weighed as such, and then dissolved in a concentrated solution of potassium sulphide. From this, after strong dilution, antimony trisulphide was thrown down by means of dilute sulphuric acid. After thorough washing, this sulphide was oxidized by hydrogen peroxide, by Classen's method, and the sulphur in it was weighed as barium sulphate. The ratio measured, therefore, was  $2\text{Sb} : 3\text{BaSO}_4$ , and the data were as follows. The  $\text{BaSO}_4$  equivalent to 100 parts of  $\text{Sb}$  is the ratio stated :

<i>Sb Taken.</i>	<i>BaSO<sub>4</sub> Found.</i>	<i>Ratio.</i>
1.4921	4.3325	290.362
.6132	1.7807	290.394
.5388	1.5655	290.553
1.2118	3.5205	290.518
.9570	2.7800	290.491
.6487	1.8855	290.349
.7280	2.1100	289.835
.9535	2.7655	290.036
1.0275	2.9800	290.024
.9635	2.7080	290.399
.9255	2.6865	290.275
.7635	2.2175	290.438

Mean, 290.306,  $\pm .0436$

We have now before us the following ratios, good and bad, from which to calculate the atomic weight of antimony. The single results obtained by Weber and by Unger, being unimportant, are not included :

\* Ber. Deutsch. Chem. Gesell., 16, 1942. 1883.

- (1.) Percentage of S in  $\text{Sb}_2\text{S}_3$ , 28.5385,  $\pm .0023$
- (2.) Percentage of Sb in  $\text{Sb}_2\text{O}_3$ , 79.283,  $\pm .009$
- (3.) O needed to oxidize 100 parts  $\text{SbCl}_3$ , 7.0294,  $\pm .0024$
- (4.) O needed to oxidize 100 parts  $\text{Sb}_2\text{O}_3$ , 10.953,  $\pm .0075$
- (5.) O needed to oxidize 100 parts Sb, 13.079,  $\pm .0096$
- (6.)  $\text{K}_2\text{Cr}_2\text{O}_7$  : tartar emetic : : 100 : 337.30,  $\pm .29$
- (7.)  $\text{Ag}_3$  :  $\text{SbCl}_3$  : : 100 : 70.512,  $\pm .021$
- (8.)  $3\text{AgCl}$  :  $\text{SbCl}_3$  : : 100 : 53.2311,  $\pm .008$
- (9.)  $\text{Ag}_3$  :  $\text{SbBr}_3$  : : 100 : 111.114,  $\pm .0014$
- (10.)  $3\text{AgBr}$  :  $\text{SbBr}_3$  : : 100 : 63.830,  $\pm .008$
- (11.)  $3\text{AgI}$  :  $\text{SbI}_3$  : : 100 : 71.060,  $\pm .023$
- (12.)  $\text{Cu}_3$  :  $\text{Sb}_2$  : : 100 : 128.259,  $\pm .0077$
- (13.)  $\text{Ag}_3$  : Sb : : 100 : 37.452,  $\pm .0119$
- (14.)  $\text{Sb}_2$  :  $3\text{BaSO}_4$  : : 100 : 290.306,  $\pm .0436$

In the reduction of these ratios a considerable number of antecedent atomic weights are required, thus :

O = 15.879, $\pm .0003$	C = 11.920, $\pm .0004$
Ag = 107.108, $\pm .0031$	Cu = 63.119, $\pm .0015$
Cl = 35.179, $\pm .0048$	Ba = 136.392, $\pm .0086$
Br = 79.344, $\pm .0062$	Cr = 51.742, $\pm .0034$
I = 125.888, $\pm .0069$	AgCl = 142.287, $\pm .0037$
K = 38.817, $\pm .0051$	AgBr = 186.452, $\pm .0054$
S = 31.828, $\pm .0015$	AgI = 232.996, $\pm .0062$

Three of the ratios give the molecular weight of antimony trichloride, and two give corresponding values for the bromide. These values may be combined, as follows: First, for the chloride—

From (3) .....	$\text{SbCl}_3 = 225.894, \pm .0771$
From (7) .....	" = 226.572, $\pm .0678$
From (8) .....	" = 227.223, $\pm .0347$
General mean .....	$\text{SbCl}_3 = 226.924, \pm .0286$

Hence Sb = 121.387,  $\pm .0321$ .

For the bromide we have—

From (9).....	$\text{SbBr}_3 = 357.036, \pm .0113$
From (10).....	" = 357.037, $\pm .0250$
General mean.....	$\text{SbBr}_3 = 357.036, \pm .0103$

Hence Sb = 119.005,  $\pm .0212$ .

All the data yield eleven values for antimony, which are arranged below in the order of their magnitude :

1. From tartar emetic, ratio (6).....	Sb = 118.024, $\pm$ .2827
2. From $\text{SbBr}_3$ . ....	" = 119.005, $\pm$ .0212
3. From $\text{SbI}_3$ , ratio (11).....	" = 119.037, $\pm$ .1626
4. From $\text{Sb}_2\text{S}_3$ , ratio (1)....	" = 119.548, $\pm$ .0069
5. From ratio (14).....	" = 119.737, $\pm$ .0188
6. From ratio (13).....	" = 120.342, $\pm$ .0384
7. From ratio (4).....	" = 121.155, $\pm$ .1000
8. From $\text{SbCl}_3$ .....	" = 121.387, $\pm$ .0321
9. From ratio (5).....	" = 121.408, $\pm$ .0891
10. From ratio (12).....	" = 121.434, $\pm$ .0078
11. From $\text{Sb}_2\text{O}_4$ , ratio (2).....	" = 121.542, $\pm$ .0546
<hr/>	
General mean.....	Sb = 120.299, $\pm$ .0047

If  $\text{O} = 16$ , this becomes  $\text{Sb} = 121.218$ .

Among these figures the discordance is so great that the mathematical combination has no real value. We must base our judgment in this case mainly upon chemical evidence, and this, as shown in the investigations of Cooke and of Schneider, favors a lower rather than a higher value for the atomic weight of antimony. Dumas' work was affected by constant errors which are now known, and Dexter's data are also presumably in the wrong. A general mean of values 2, 3, 4, and 5 gives  $\text{Sb} = 119.521$ ,  $\pm$  .0062, or, if  $\text{O} = 16$ ,  $\text{Sb} = 120.432$ . Even now the range of uncertainty is greater than it should be, but none of the four values combined can be accepted exclusively or rejected without more evidence. This result, therefore, should be adopted until new determinations, of a more conclusive nature, have been made.



## BISMUTH.

Early in the century the combining weight of bismuth was approximately fixed through the experiments of Lagerhjelm.\* Effecting the direct union of bismuth and sulphur, he found that ten parts of the metal yield the following quantities of trisulphide:

12.2520
12.2065
12.2230
12.2465
<hr/>
Mean, 12.2320

Hence Bi = 215 in round numbers, a value now known to be much too high. Lagerhjelm also oxidized bismuth with nitric acid, and, after ignition, weighed the trioxide thus formed. Ten parts of metal gave the following quantities of  $\text{Bi}_2\text{O}_3$ :

11.1382
11.1275
<hr/>
Mean, 11.13285

Hence, if O = 16, Bi = 211.85, a figure still too high.

In 1851 the subject of the atomic weight of bismuth was taken up by Schneider,† who, like Lagerhjelm, studied the oxidation of the metal with nitric acid. The work was executed with a variety of experimental refinements, by means of which every error due to possible loss of material was carefully avoided. For full details the original paper must be consulted; there is only room in these pages for the actual results, as follows. The figures represent the percentages of Bi in  $\text{Bi}_2\text{O}_3$ :

89.652
89.682
89.644
89.634
89.656
89.666
89.655
89.653
<hr/>
Mean, 89.6552, $\pm .0034$

Hence, if O = 16, Bi = 208.05.

Next in order are the results obtained by Dumas.‡ Bismuth tri-

\* Annals of Philosophy, 4, 358. 1814. Adopted by Berzelius.

† Poggend. Annalen, 82, 303. 1851.

‡ Ann. Chim. Phys. (3), 55, 176. 1859.

chloride was prepared by the action of dry chlorine upon bismuth, and repeatedly rectified by distillation over bismuth powder. The product was weighed in a closed tube, dissolved in water, and precipitated with sodium carbonate. In the filtrate, after strongly acidulating with nitric acid, the chlorine was precipitated by a known amount of silver. The figures in the third column show the quantities of  $\text{BiCl}_3$  proportional to 100 parts of silver:

3.506	gm.	$\text{BiCl}_3$	=	3.545	gm.	Ag.	98.900
1.149	"			1.168	"		98.373
1.5965	"			1.629	"		98.005
2.1767	"			2.225	"		97.829
3.081	"			3.144	"		97.996
2.4158	"			2.470	"		97.806
1.7107	"			1.752	"		97.643
3.523	"			3.6055	"		97.712
5.241	"			5.361	"		97.762
							Mean, 98.003, $\pm .090$

Hence, with  $\text{Ag} = 108$  and  $\text{Cl} = 35.5$ ,  $\text{Bi} = 211.03$ .

The first three of the foregoing experiments were made with slightly discolored material. The remaining six percentages give a mean of 97.791, whence, on the same basis as before,  $\text{Bi} = 110.79$ . Evidently these results are now of slight value, for it is probable that the chloride of bismuth, like the corresponding antimony compound, contained traces of oxychloride. This assumption fully accounts for the discordance between Dumas' determination and the determinations of Schneider and of still more recent investigators.

In 1883 Marignac\* took up the subject, attacking the problem by two methods. His point of departure was commercial subnitrate of bismuth, which was purified by re-solution and reprecipitation, and from which he prepared the oxide. First, bismuth trioxide was reduced by heating in hydrogen, beginning with a moderate temperature and closing the operation at redness. The results were as follows, with the percentage of Bi in  $\text{Bi}_2\text{O}_3$  added:

2.6460	gm.	$\text{Bi}_2\text{O}_3$	lost	0.2730	gm.	O.	89.683	per cent.
6.7057	"			.6910	"		89.696	"
3.6649	"			.3782	"		89.681	"
5.8024	"			.5981	"		89.692	"
5.1205	"			.5295	"		89.658	"
5.5640	"			.5742	"		89.680	"
							Mean, 89.682, $\pm .0036$	

Hence, if  $\text{O} = 16$ ,  $\text{Bi} = 208.60$ .

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\* Arch. Sci. Phys. et Nat. (3), 10, 10.

Marignac's second method of determination was by conversion of the oxide into the sulphate. The oxide was dissolved in nitric acid, and then sulphuric acid was added in slight excess from a graduated tube. The mass was evaporated to dryness with great care, and finally heated over a direct flame until fumes of  $\text{SO}_3$  no longer appeared. The third column gives the sulphate formed from 100 parts of oxide:

2.6503	$\text{Bi}_2\text{O}_3$	gave	4.0218	$\text{Bi}_2(\text{SO}_4)_3$ .	Ratio, 151.749
2.8025	"		4.2535	"	" 151.775
2.710	"		4.112	"	" 151.734
2.813	"		4.267	"	" 151.688
2.8750	"		4.3625	"	" 151.739
2.7942	"		4.2383	"	" 151.682

Mean, 151.728,  $\pm$  .0099

Hence, with  $\text{O} = 16$  and  $\text{S} = 32.06$ ,  $\text{Bi} = 208.16$ .

This result needs to be studied in the light of Bailey's observation,\* that bismuth sulphate has a very narrow range of stability. It loses the last traces of free sulphuric acid at  $405^\circ$ , and begins to decompose at  $418^\circ$ , so that the foregoing ratio is evidently uncertain. The concordance of the data, however, is favorable to it.

The next determination of this atomic weight was by Löwe,† who oxidized the metal with nitric acid, and reduced the nitrate to oxide by ignition. Special care was taken to prepare bismuth free from arsenic, and the oxide was fused before weighing. In the paper just quoted Bailey calls attention to the volatility of bismuth oxide, which doubtless accounts for the low results found in this investigation. The data are as follows:

<i>Bi Taken.</i>	<i><math>\text{Bi}_2\text{O}_3</math> Found.</i>	<i>Per cent. Bi.</i>
11.309	12.616	89.640
12.2776	13.694	89.656

Mean, 89.648,  $\pm$  .0040

Hence, if  $\text{O} = 16$ ,  $\text{Bi} = 207.84$ .

In Classen's‡ work upon the atomic weight of bismuth, the metal itself was first carefully investigated. Commercial samples, even those which purported to be pure, were found to be contaminated with lead and other impurities, and these were not entirely removable by many successive precipitations as subnitrate. Finally, pure bismuth was obtained by an electrolytic process, and this was converted into oxide by means of nitric acid and subsequent ignition to incipient fusion. Results as follows, with the percentage of Bi in  $\text{Bi}_2\text{O}_3$  added:

\* Journ. Chem. Soc., 51, 676.

† Zeit. Anal. Chem., 22, 498.

‡ Ber. Deutsch. Chem. Gesell., 23, 938. 1890.

<i>Bi Taken.</i>	<i>Bi<sub>2</sub>O<sub>3</sub> Found.</i>	<i>Per cent. Bi.</i>
25.0667	27.9442	89.703
21.0691	23.4875	89.7035
27.2596	30.3922	89.693
36.5195	40.7131	89.700
27.9214	31.1295	89.6944
32.1188	35.8103	89.692
30.1000	33.5587	89.694
26.4825	59.5257	89.693
19.8008	22.0758	89.695

Mean, 89.696,  $\pm$  .0009

Hence, if O = 16, Bi = 208.92, or, reduced to vacuum standards, 208.90.

Classen's paper was followed by a long controversy between Schneider and Classen,\* in which the former upheld the essential accuracy of the work done by Marignac and himself. Schneider had started out with commercial bismuth, and Classen found that the commercial bismuth which he met with was impure. Schneider, by various analyses, showed that other samples of bismuth were so nearly pure that the common modes of purification were adequate; but Classen replied that the original sample used by Schneider in his atomic weight investigation had not been reexamined. Accordingly, Schneider published a new series of determinations† made by the old method, but with metal which had been scrupulously purified. Results as follows:

<i>Bi.</i>	<i>Bi<sub>2</sub>O<sub>3</sub>.</i>	<i>Per cent Bi.</i>
5.0092	5.5868	89.661
3.6770	4.1016	89.648
7.2493	8.0854	89.659
9.2479	10.3142	89.662
6.0945	6.7979	89.653
12.1588	13.5610	89.660

Mean, 89.657,  $\pm$  .0015

Hence with O = 16, Bi = 208.05, a confirmation of the earlier determinations.

Although the results so far are not final, a combination of the data relative to bismuth oxide is not without interest.

1. Lagerhjelm .....	89.865, $\pm$ .0650
2. Schneider, 1851 .....	89.655, $\pm$ .0034
3. Marignac .....	89.682, $\pm$ .0036
4. Löwe .....	89.648, $\pm$ .0040
5. Classen .....	89.696, $\pm$ .0009
6. Schneider, 1894 .....	89.657, $\pm$ .0015
General mean .....	89.681, $\pm$ .0007

\* Journ. für Prakt. Chem. (2), 42, 553; 43, 133; and 44, 23 and 411.

† Journ. für Prakt. Chem. (2), 50, 461. 1894.

Omitting the first and fifth means, the other data give a general mean percentage of 89.659,  $\pm .0012$ .

The ratios now before us are as follows :

- (1.) Percentage of Bi in  $\text{Bi}_2\text{O}_3$ , 89.681,  $\pm .0007$
- (2.)  $\text{Bi}_2\text{O}_3 : \text{Bi}_2(\text{SO}_4)_3 :: 100 : 151.728$ ,  $\pm .0099$
- (3.)  $3\text{Ag} : \text{BiCl}_3 :: 100 : 98.003$ ,  $\pm .090$

For computation we have—

O = 15.879, $\pm .0003$	Ag = 107.108, $\pm .0031$
S = 31.828, $\pm .0015$	Cl = 35.179, $\pm .0048$

Hence, reducing the ratios—

From (1) .....	Bi = 207.003, $\pm .0150$
From (2) ....	“ = 206.613, $\pm .0444$
From (3) .....	“ = 209.370, $\pm .2847$
General mean...	Bi = 206.971, $\pm .0142$

If O = 16, Bi = 208.548.

Classen's data alone give Bi = 207.389, or, with O = 16, 208.969. Omitting this set of determinations and rejecting Dumas', the remaining data give—

From $\text{Bi}_2\text{O}_3$ .....	Bi = 206.512, $\pm .0244$
From $\text{Bi}_2(\text{SO}_4)_3$ .....	“ = 206.613, $\pm .0444$
General mean .....	Bi = 206.536, $\pm .0214$

If O = 16, this becomes Bi = 208.11. Between this figure and Classen's, future investigation must decide. The confirmation afforded by the sulphate series is in favor of the lower value.

## COLUMBIUM.\*

The atomic weight of this metal has been determined by Rose, Hermann, Blomstrand, and Marignac. Rose † analyzed a compound which he supposed to be chloride, but which, according to Rammelsberg, ‡ must have been nearly pure oxychloride. If it was chloride, then the widely varying results give approximately  $Cb = 122$ ; if it was oxychloride, the value becomes nearly 94. If it was chloride, it was doubtless contaminated with tantalum compounds.

Hermann's § results seem to have no present value, and Blomstrand's || are far from concordant. The latter chemist studied columbium pentachloride and sodium columbate. In the first case he weighed the columbium as columbium pentoxide, and the chlorine as silver chloride, the oxide being determined by several distinct processes. In some cases it was thrown down by water, in others by sulphuric acid, and in still others by sodium carbonate or ammonia jointly with sulphuric acid. The weights given are as follows:

$CbCl_5$ .	$Cb_2O_5$ .	$AgCl$ .
.591	.294	.....
.8085	.401	2.085
.633	.317	.....
.195	.0974	.500
.507	.2505	1.302
.9415	.472	2.454
.563	.2796	.....
.9385	.4675	2.465
.4788	.2378	.....
.408	.204	1.067
.9065	.4515	.....

Hence the subjoined percentages, and the ratios  $5AgCl : CbCl_5 :: 100 : x$ , and  $5AgCl : Cb_2O_5 :: 100 : x$ .

<i>Per cent.</i> $Cb_2O_5$ .	$AgCl : CbCl_5$ .	$AgCl : Cb_2O_5$ .
49.788	.....	.....
49.598	38.777	19.233
50.079	... .	.....
49.949	39.000	19.435
49.408	38.940	19.240
50.135	38.366	19.234

\* This name has priority over the more generally accepted "niobium," and therefore deserves preference.

† Poggend. Annal., 104, 439. 1858.

‡ Poggend. Annal., 136, 353. 1869.

§ Journ. für Prakt. Chem., 68, 73. 1856.

|| Acta Univ. Lund, 1864.

49.662	.....	.....
49.813	38.073	18.966
49.666	.....	.....
50.000	38.238	19.119
49.807	.....	.....
Mean, 49.806, $\pm .045$	Mean, 38.566, $\pm .108$	Mean, 19.205, $\pm .043$

From these means the atomic weight of columbium may be computed, thus :

From $2\text{CbCl}_3 : \text{Cb}_2\text{O}_5$ .....	Cb = 95.397
From $\text{CbCl}_3 : 5\text{AgCl}$ .....	" = 98.477
From $5\text{AgCl} : \text{Cb}_2\text{O}_5$ .....	" = 96.933,

when  $\text{O} = 15.879$ ,  $\text{Ag} = 107.108$ , and  $\text{Cl} = 35.179$ .

The series upon sodium columbate, which salt was decomposed with sulphuric acid, both  $\text{Cb}_2\text{O}_5$  and  $\text{Na}_2\text{SO}_4$  being weighed, is too discordant for discussion. The exact nature of the salt studied is not clear, and the data given, when transformed into the ratio  $\text{Na}_2\text{SO}_4 : \text{Cb}_2\text{O}_5 : : 100 : x$ , give values for  $x$  ranging from 151.65 to 161.20. Further consideration of this series would therefore be useless. It seems highly probable that Blomstrand's materials were not entirely free from tantalum, however, since the atomic weight of columbium derived from his analyses of the chloride are evidently too high.

Marignac\* made about twenty analyses of the potassium fluoxycolumbate,  $\text{CbOF}_3 \cdot 2\text{KF} \cdot \text{H}_2\text{O}$ . 100 parts of this salt give the following percentages :

$\text{Cb}_2\text{O}_5$ .....	Extremes	44.15 to 44.60	Mean, 44.36
$\text{K}_2\text{SO}_4$ .....	"	57.60 " 58.05	
$\text{H}_2\text{O}$ .....	"	5.75 " 5.98	
F.....	"	30.62 " 32.22	

From the mean percentage of  $\text{Cb}_2\text{O}_5$ ,  $\text{Cb} = 92.852$ . If  $\text{O} = 16$ , this becomes 93.56.

From the mean between the extremes given for  $\text{K}_2\text{SO}_4$ ,  $\text{Cb} = 93.192$ . If  $\text{O} = 16$ , this becomes 93.90.

As Deville and Troost's† results for the vapor density of the chloride and oxychloride agree fairly well with  $\text{Cb} = 94$ , we may adopt this value as approximately correct. The mean of the two values computed from Marignac's data is 93.022 when  $\text{H} = 1$ , and 93.73 when  $\text{O} = 16$ .

\* Arch. Sci. Phys. Nat. (2), 23. 1865.

† Compt. Rend., 56, 891. 1863.

## TANTALUM.

The results obtained for the atomic weight of this metal by Berzelius,\* Rose,† and Hermann‡ may be fairly left out of account as valueless. These chemists could not have worked with pure preparations, and their data are sufficiently summed up in Beeker's "Digest."

Blomstrand's determinations,§ as in the case of columbium, were made upon the pentachloride. His weights are as follows:

$TaCl_5$ .	$Ta_2O_5$ .	$AgCl$ .
.9808	.598	.....
1.4262	.867	2.906
2.5282	1.5375	5.0105
1.0604	.6455	2.156
2.581	1.577	.....
.8767	.534	.....

Hence the subjoined percentages of  $Ta_2O_5$  from  $TaCl_5$ , and the ratios  $5AgCl : TaCl_5 :: 100 : x$ , and  $5AgCl : Ta_2O_5 :: 100 : x$ .

<i>Per cent.</i> $Ta_2O_5$ .	$AgCl : TaCl_5$ .	$AgCl : Ta_2O_5$ .
60.971	.....	.....
60.791	49.078	29.835
60.814	50.458	30.685
60.873	49.297	29.940
60.960	.....	.....
60.924	.....	.....
Mean, 60.889, $\pm .0208$	49.611, $\pm .289$	30.153, $\pm .180$

From these ratios we get for the atomic weight of tantalum:

From per cent. $Ta_2O_5$ .....	$Ta = 172.342$
From $5AgCl : TaCl_5$ .....	" = 177.055
From $5AgCl : Ta_2O_5$ .....	" = 174.821

These results are too low. Probably Blomstrand's material still contained some columbium.

In 1866 Marignac's determinations appeared.|| He made four analyses of a pure potassium fluotantalate, and four more experiments upon the ammonium salt. The potassium compound,  $K_2TaF_7$ , was treated with sulphuric acid, and the mixture was then evaporated to dryness. The potassium sulphate was next dissolved out by water, while the residue

\* Poggend. Annalen, 4, 14. 1825.

† Poggend. Annalen, 99, 80. 1856.

‡ Journ. für Prakt. Chem., 70, 193. 1857.

§ Acta Univ. Lund, 1864

|| Arch. Sci. Phys. Nat. (2), 26, 89. 1866.



was ignited and weighed as  $Ta_2O_5$ . 100 parts of the salt gave the following quantities of  $Ta_2O_5$  and  $K_2SO_4$ :

$Ta_2O_5$ .	$K_2SO_4$ .
56.50	44.37
56.75	44.35
56.55	44.22
<u>56.56</u>	<u>44.24</u>
Mean, 56.59, $\pm .037$	Mean, 44.295, $\pm .026$

From these figures, 100 parts of  $K_2SO_4$  correspond to the subjoined quantities of  $Ta_2O_5$ :

127.338
127.960
128.178
<u>127.848</u>
Mean, 127.831, $\pm .120$

The ammonium salt,  $(NH_4)_2TaF_7$ , ignited with sulphuric acid, gave these percentages of  $Ta_2O_5$ . The figures are corrected for a trace of  $K_2SO_4$  which was always present:

63.08
63.24
63.27
<u>63.42</u>
Mean, 63.25, $\pm .047$

Hence we have four values for Ta:

From potassium salt, per cent. $Ta_2O_5$ . . . . .	Ta = 182.336
From potassium salt, per cent. $K_2SO_4$ . . . . .	" = 180.496
From potassium salt, $K_2SO_4 : Ta_2O_5$ . . . . .	" = 181.422
From ammonium salt, per cent. $Ta_2O_5$ . . . . .	" = 181.559
Average . . . . .	<u>Ta = 181.453</u>

Or, if O = 16, Ta = 182.836.

These values are computed with O = 15.879, K = 38.817, S = 31.828, N = 13.935, and F = 18.912.

## CHROMIUM.

Concerning the atomic weight of chromium there has been much discussion, and many experimenters have sought to establish the true value. The earliest work upon it having any importance was that of Berzelius,\* in 1818 and 1826, which led to results much in excess of the correct figure. His method consisted in precipitating a known weight of lead nitrate with an alkaline chromate and weighing the lead chromate thus produced. The error in his determination arose from the fact that lead chromate, except when thrown down from very dilute solutions, carries with it minute quantities of alkaline salts, and so has its apparent weight notably increased. When dilute solutions are used, a trace of the precipitate remains dissolved, and the weight obtained is too low. In neither case is the method trustworthy.

In 1844 Berzelius' results were first seriously called in question. The figure for chromium deduced from his experiments was somewhat over 56; but Peligot† now showed, by his analyses of chromous acetate and of the chlorides of chromium, that the true number was near 52.5. Unfortunately, Peligot's work, although good, was published with insufficient details to be useful here. For chromous acetate he gives the percentages of carbon and hydrogen, but not the actual weights of salt, carbon dioxide, and water from which they were calculated. His figures vary considerably, moreover—enough to show that their mean would carry but little weight when combined with the more explicit data furnished by other chemists.

Jacquelain's‡ work we may omit entirely. He gives an atomic weight for chromium which is notoriously too low (50.1), and prints none of the numerical details upon which his result rests. The researches which particularly command our attention are those of Berlin, Moberg, Lefort, Wildenstein, Kessler, Siewert, Baubigny, Rawson, and Meineke.

Among the papers upon the atomic weight under consideration that by Berlin is one of the most important.§ His starting point was normal silver chromate; but in one experiment the dichromate  $\text{Ag}_2\text{Cr}_2\text{O}_7$  was used. These salts, which are easily obtained in a perfectly pure condition, were reduced in a large flask by means of hydrochloric acid and alcohol. The chloride of silver thus formed was washed by decantation, dried, fused, and weighed without transfer. The united washings were supersaturated with ammonia, evaporated to dryness, and the residue treated with hot water. The resulting chromic oxide was then collected upon a filter, dried, ignited, and weighed. The results were as follows:

\* Schweigg. Journ., 22, 53, and Poggend. Annal., 8, 22.

† Compt. Rend., 19, 609, and 734; 20, 1187; 21, 74.

‡ Compt. Rend., 24, 679. 1847.

§ Journ. für Prakt. Chem., 37, 509, and 38, 149. 1846.

4.6680	gm.	$\text{Ag}_2\text{CrO}_4$	gave	4.027	gm.	$\text{AgCl}$	and	1.0754	gm.	$\text{Cr}_2\text{O}_3$ .
3.4568		"		2.983		"		.7960		"
2.5060		"		2.1605		"		.5770		"
2.1530		"		1.8555		"		.4945		"
4.5335	gm.	$\text{Ag}_2\text{Cr}_2\text{O}_7$	gave	2.8692		"		1.5300		"

From these weighings three values are calculable for the atomic weight of chromium. The three ratios upon which these values depend we will consider separately, taking first that between the chromic oxide and the original silver salt. In the four analyses of the normal chromate the percentages of  $\text{Cr}_2\text{O}_3$  deducible from Berlin's weighings are as follows:

23.037
23.027
23.025
22.968
<hr/>

Mean, 23.014,  $\pm .011$

And from the single experiment with  $\text{Ag}_2\text{Cr}_2\text{O}_7$  the percentage of  $\text{Cr}_2\text{O}_3$  was 35.306.

For the ratio between  $\text{Ag}_2\text{CrO}_4$  and  $\text{AgCl}$ , putting the latter at 100, we have for the former:

115.917
115.883
115.992
116.033
<hr/>

Mean, 115.956,  $\pm .023$

In the single experiment with dichromate 100  $\text{AgCl}$  is formed from 151.035  $\text{Ag}_2\text{Cr}_2\text{O}_7$ .

Finally, for the ratio between  $\text{AgCl}$  and  $\text{Cr}_2\text{O}_3$ , the five experiments of Berlin give, for 100 parts of the former, the following quantities of the latter:

26.705
26.685
26.707
26.650
26.662
<hr/>

Mean, 26.682,  $\pm .0076$

These results will be discussed, in connection with the work of other investigators, at the end of this chapter.

In 1848 the researches of Moberg\* appeared. His method simply consisted in the ignition of anhydrous chromic sulphate and of ammonium chrome alum, and the determination of the amount of chromic

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\* Journ. für Prakt. Chem., 43, 114.

oxide thus left as residue. In the sulphate,  $\text{Cr}_2(\text{SO}_4)_3$ , the subjoined percentages of  $\text{Cr}_2\text{O}_3$  were found. The braces indicate two different samples of material, to which, however, we are justified in ascribing equal value:

.542	gram. sulphate gave	.212	gram. $\text{Cr}_2\text{O}_3$ .	39.114	per cent.	}
1.337	"	.523	"	39.117	"	
.5287	"	.207	"	39.153	"	}
1.033	"	.406	"	39.303	"	
.868	"	.341	"	39.286	"	}

Mean, 39.1946,  $\pm .0280$

From the alum,  $\text{NH}_4\text{Cr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , we have these percentages of  $\text{Cr}_2\text{O}_3$ . The first series represents a salt long dried under a bell jar at a temperature of  $18^\circ$ . The crystals taken were clear and transparent, but may possibly have lost traces of water,\* which would tend to increase the atomic weight found for chromium. In the second series the salt was carefully dried between folds of filter paper, and results were obtained quite near those of Berlin. Both of these series are discussed together, neither having remarkable value:

1.3185	gram. alum gave	.213	gram. $\text{Cr}_2\text{O}_3$ .	16.155	per cent.
.7987	"	.129	"	16.151	"
1.0185	"	.1645	"	16.151	"
1.0206	"	.1650	"	16.167	"
.8765	"	.1420	"	16.201	"
.7680	"	.1242	"	16.172	"
1.6720	"	.2707	"	16.190	"
.5410	"	.0875	"	16.174	"
1.2010	"	.1940	"	16.153	"
1.0010	"	.1620	"	16.184	"
.7715	"	.1235	"	16.007	"
1.374	"	.2200	"	16.012	"

Mean, 16.143,  $\pm .0125$

The determinations made by Lefort † are even less valuable than those by Moberg. This chemist started out from pure barium chromate, which, to thoroughly free it from moisture, had been dried for several hours at  $250^\circ$ . The chromate was dissolved in pure nitric acid, the barium thrown down by sulphuric acid, and the precipitate collected upon a filter, dried, ignited, and weighed in the usual manner. The natural objection to the process is that traces of chromium may be carried down with the sulphate, thus increasing its weight. In fact, Lefort's results are somewhat too high. Calculated from his weighings, 100 parts of  $\text{BaSO}_4$  correspond to the amounts of  $\text{BaCrO}_4$  given in the third column:

\* This objection is suggested by Berlin in a note upon Lefort's paper. Journ. für Prakt. Chem., 71, 191.

† Journ. für Prakt. Chem., 51, 261. 1850.

1.2615	gram. BaCrO <sub>4</sub> gave	1.1555	gram. BaSO <sub>4</sub> .	109.174
1.5895	"	1.4580	"	109.019
2.3255	"	2.1340	"	108.974
3.0390	"	2.7855	"	109.101
2.3480	"	2.1590	"	108.754
1.4230	"	1.3060	"	108.708
1.1975	"	1.1005	"	108.814
3.4580	"	3.1690	"	109.119
2.0130	"	1.8430	"	109.224
3.5570	"	3.2710	"	108.744
1.6470	"	1.5060	"	109.363
1.8240	"	1.6725	"	109.058
1.6950	"	1.5560	"	108.933
2.5960	"	2.3870	"	108.756

Mean, 108.9815,  $\pm$  .0369

Wildenstein,\* in 1853, also made barium chromate the basis of his researches. A known weight of pure barium chloride was precipitated by a neutral alkaline chromate, and the precipitate allowed to settle until the supernatant liquid was perfectly clear. The barium chromate was then collected on a filter, washed with hot water, dried, gently ignited, and weighed. Here again arises the objection that the precipitate may have retained traces of alkaline salts, and again we find deduced an atomic weight which is too high. One hundred parts BaCrO<sub>4</sub> correspond to BaCl<sub>2</sub> as follows :

81.87	81.57
81.80	81.75
81.61	81.66
81.78	81.83
81.52	81.66
81.84	81.80
81.85	81.66
81.70	81.85
81.68	81.57
81.54	81.83
81.66	81.71
81.55	81.63
81.81	81.56
81.86	81.58
81.54	81.67
81.68	81.84

Mean, 81.702,  $\pm$  .014

Next in order we have to consider two papers by Kessler, who employed a peculiar volumetric method entirely his own. In brief, he compared the oxidizing power of potassium dichromate with that of the chlorate, and from his observations deduced the ratio between the molecular weights of the two salts.

† Journ. für Prakt. Chem., 59, 27.

In his earlier paper\* the mode of procedure was about as follows: The two salts, weighed out in quantities having approximate chemical equivalency, were placed in two small flasks, and to each was added 100 cc. of a ferrous chloride solution and 30 cc. hydrochloric acid. The ferrous chloride was added in trifling excess, and, when action ceased, the amount unoxidized was determined by titration with a standard solution of dichromate. As in each case the quantity of ferrous chloride was the same, it became easy to deduce from the data thus obtained the ratio in question. I have reduced all of his somewhat complicated figures to a simple common standard, and give below the amount of chromate equivalent to 100 of chlorate:

120.118
120.371
120.138
120.096
120.241
120.181
<hr/>
Mean, 120.191, $\pm$ .028

In his later paper† Kessler substituted arsenic trioxide for the iron solution. In one series of experiments the quantity of dichromate needed to oxidize 100 parts of the arsenic trioxide was determined, and in another the latter substance was similarly compared with the chlorate. The subjoined columns give the quantity of each salt proportional to 100 of  $\text{As}_2\text{O}_3$ :

$K_2Cr_2O_7$ .	$KClO_3$ .
98.95	41.156
98.94	41.116
99.17	41.200
98.98	41.255
99.08	41.201
99.15	41.086
<hr/>	41.199
Mean, 99.045, $\pm$ .028	41.224
	41.161
	41.193
	41.149
	41.126
	<hr/>
	Mean, 41.172, $\pm$ .009

Reducing the later series to the standard of the earlier, the two combine as follows:

(1) $2\text{KClO}_3 : \text{K}_2\text{Cr}_2\text{O}_7 :: 100 : 120.191, \pm .028$	
(2) $2\text{KClO}_3 : \text{K}_2\text{Cr}_2\text{O}_7 :: 100 : 120.282, \pm .043$	
<hr/>	
General mean, . . . . . 120.216, $\pm$ .0235	

\* Poggend. Annalen, 95, 208 1855.

† Poggend. Annalen, 113, 137. 1861.

Siewert's determinations, which do not seem to have attracted general attention, were published in 1861.\* He, reviewing Berlin's work, found that upon reducing silver chromate with hydrochloric acid and alcohol, the chromic chloride solution always retained traces of silver chloride dissolved in it. These could be precipitated by dilution with water; but, in Berlin's process, they naturally came down with the chromium hydroxide, making the weight of the latter too high; hence too large a value for the atomic weight of chromium. In order to find a more correct value Siewert resorted to the analysis of sublimed, violet, chromic chloride. This salt he fused with sodium carbonate and a little nitre, treated the fused mass with water, and precipitated from the resulting solution the chlorine by silver nitrate in presence of nitric acid. The weight of the silver chloride thus obtained, estimated after the usual manner, gave means for calculating the atomic weight of chromium. His figures, reduced to a common standard, give, as proportional to 100 parts of chloride of silver, the quantities of chromic chloride stated in the third of the subjoined columns:

.2367	gram. $\text{CrCl}_3$	gave .6396	gram. $\text{AgCl}$ .	37.007
.2946	"	.7994	"	36.853
.2593	"	.7039	"	36.838
.4935	"	1.3395	"	36.842
.5850	"	1.5884	"	36.830
.6511	"	1.76681	"	36.852
.5503	"	1.49391	"	36.836

Mean, 36.865,  $\pm .0158$

The first of these figures varies so widely from the others that we are justified in rejecting it, in which case the mean becomes 36.842,  $\pm .0031$ .

Siewert also made two analyses of silver dichromate by the following process. The salt, dried at  $120^\circ$ , was dissolved in nitric acid. The silver was then thrown down by hydrochloric acid, and, in the filtrate, chromium hydroxide was precipitated by ammonia. Reduced to a uniform standard, we find from his results, corresponding to 100 parts of  $\text{AgCl}$ ,  $\text{Ag}_2\text{Cr}_2\text{O}_7$  as in the last column:

.7866	gram. $\text{Ag}_2\text{Cr}_2\text{O}_7$	gave .52202 $\text{AgCl}$ and .2764 $\text{Cr}_2\text{O}_3$ .	150.684
1.089	"	.72249 " .3840 "	150.729

Berlin's single determination of this ratio gave 151.035. Taking all three values together as one series, they give a mean of 150.816,  $\pm .074$ .

Siewert's percentages of  $\text{Cr}_2\text{O}_3$  obtained from  $\text{Ag}_2\text{Cr}_2\text{O}_7$  are as follows, calculated from the above weighings:

35.139
35.262
Mean, 35.2005, $\pm .0415$

\* Zeit. Gesammt. Wissenschaften, 17, 539.

Combining, as before, with Berlin's single result, giving the latter equal weight with one of these, we have a general mean of 35.236,  $\pm .0335$ .

For the ratio between silver chloride and chromic oxide, Siewert's two analyses of the dichromate come out as follows. For 100 parts of AgCl we have of  $\text{Cr}_2\text{O}_3$ :

$$\begin{array}{r} 52.948 \\ 53.150 \\ \hline \text{Mean, } 53.049, \pm .068 \end{array}$$

This figure, reduced to the standard of Berlin's work on the monochromate, becomes 26.525,  $\pm .034$ . Berlin's mean was 26.682,  $\pm .0076$ . The two means, combined, give a general mean of 26.676,  $\pm .074$ .

By Baubigny\* we have only three experiments upon the calcination of anhydrous chromic sulphate, as follows:

1.989	gram.	$\text{Cr}_2(\text{SO}_4)_3$	gave	.7715	gram.	$\text{Cr}_2\text{O}_3$ .	38.788	per cent.
3.958		"		1.535		"	38.782	"
2.6052		"		1.0115		"	38.826	"

$$\text{Mean, } 38.799, \pm .0092$$

Moberg found for the same ratio the percentage 39.195,  $\pm .028$ . The general mean of both series, Moberg's and Baubigny's, is 38.838,  $\pm .0087$ .

In Rawson's work † ammonium dichromate was the substance studied. Weighed quantities of this salt were dissolved in water, and then reduced by hydrochloric acid and alcohol. After evaporation to dryness the mass was treated with water and ammonia, reëvaporated, dried five hours at  $140^\circ$ , and finally ignited in a muffle. The residual chromic oxide was bright green, and was tested to verify its purity. The corrected weights are as follows:

$\text{Am}_2\text{Cr}_2\text{O}_7$ .	$\text{Cr}_2\text{O}_3$ .	Per cent. $\text{Cr}_2\text{O}_3$ .
1.01275	.61134	60.365
1.08181	.65266	60.330
1.29430	.78090	60.334
1.13966	.68799	60.368
.98778	.59595	60.332
1.14319	.68987	60.346

$$\text{Mean, } 60.346, \pm .0046$$

Latest in time and most elaborate of all, we come to the determinations of the atomic weight of chromium made by Meineke, ‡ who studied the chromate and ammonio-chromate of silver, and also the dichromates of potassium and ammonium. For the latter salt he measured the same ratio that Rawson determined, but by a different method. He precipi-

\* Compt. Rend., 98, 146.

† Journ. Chem. Soc., 55, 213.

‡ Ann. d. Chem., 261, 339. 1891.



tated its solution with mercurous nitrate, and ignited the precipitate, with the subjoined results. Vacuum weights are given:

$Am_2Cr_2O_7$ .	$Cr_2O_3$ .	<i>Per cent.</i> $Cr_2O_3$ .
2.0416	1.2316	60.325
2.1618	1.3040	60.320
2.0823	1.2562	60.328
2.1913	1.3221 *	60.335
2.0970	1.2656	60.353
		Mean, 60.332, $\pm$ .0037
		Rawson found, 60.346, $\pm$ .0046
		General mean, 60.337, $\pm$ .0029

The chromate of silver,  $Ag_2CrO_4$ , and the ammonio-chromate,  $Ag_2CrO_4 \cdot 4NH_3$ , both prepared with all necessary precautions to insure purity, were first treated essentially as in Berlin's experiments, except that the traces of silver chloride held in solution by the chromic chloride were thrown out by sulphuretted hydrogen, estimated, and their amount added to the main portion. Thus the chief error in Berlin's work was avoided. I subjoin the data obtained, with vacuum standards, as usual. All of Meineke's results are so corrected:

$Ag_2CrO_4$ .	$AgCl$ .	$Cr_2O_3$ .
2.7826	2.4047	.6384
3.2627	2.8199	.7480
3.6362	3.1416	.8338
4.6781	4.0414	1.0726
3.2325	2.7930	.7411
3.9137	3.3805	.8976

Hence we have the following ratios, as in the case of Berlin's data:

<i>Per cent.</i> $Cr_2O_3$ .	100 $AgCl$ : $Ag_2CrO_4$ .	100 $AgCl$ : $Cr_2O_3$ .
22.943	115.715	26.548
22.926	115.703	26.526
22.931	115.744	26.602
22.928	115.754	26.601
22.924	115.736	26.531
22.935	115.773	26.552

Mean, 22.931,  $\pm$  .0019

Berlin, 23.014,  $\pm$  .0110

Mean, 115.737,  $\pm$  .0072

Berlin, 115.956,  $\pm$  .0230

Mean, 26.560,  $\pm$  .0093

General mean, 22.934,  $\pm$  .0018    General mean, 115.760,  $\pm$  .0069

With the ammonio-chromate Meineke found as follows:

$Ag_2CrO_4 \cdot 4NH_3$ .	$AgCl$ .	$Cr_2O_3$ .
4.1518	2.9724	.7904
4.2601	3.0592	.8125
5.9348	4.2654	1.1317

\* Calculated back from Meineke's value for Cr, to replace an evident misprint in the original.

And the ratios become—

<i>Per cent. Cr<sub>2</sub>O<sub>3</sub>.</i>	<i>100 AgCl : Salt.</i>	<i>100 AgCl : Cr<sub>2</sub>O<sub>3</sub>.</i>
19.037	139.679	26.591
19.072	139.255	26.559
19.059	139.138	26.532
<hr/>		
Mean, 19.059, $\pm$ .0074	Mean, 139.357, $\pm$ .1109	Mean, 26.561, $\pm$ .0115

The first of these three analyses is rejected by Meineke as suspicious, but for the present I shall allow it to remain. The data in the third column may now be combined with the corresponding figures from the normal chromate, as found by Meineke and his predecessors.

Berlin, .....	26.682, $\pm$ .0076
Siewert, from Ag <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> , .....	26.525, $\pm$ .0340
Meineke, from Ag <sub>2</sub> CrO <sub>4</sub> .....	26.560, $\pm$ .0093
Meineke, from Ag <sub>2</sub> CrO <sub>4</sub> .4NH <sub>3</sub> , .....	26.561, $\pm$ .0115
<hr/>	
General mean, .....	26.620, $\pm$ .0052

$$4\text{AgCl} : \text{Cr}_2\text{O}_3 :: 100 : 26.620, \pm .0052$$

Obviously, this mean is vitiated by the known error in Berlin's work, the ultimate effect of which is yet to be considered.

In all four of the salts studied by Meineke he determined volumetrically the oxygen in excess of the normal oxides by measuring the amount of iodine liberated in acid solutions. With the silver salts the process was essentially as follows: A weighed quantity of the chromate was dissolved in weak ammonia, and the solution was precipitated with potassium iodide. After the silver iodide had been filtered off, five or six grammes of potassium iodide were added to the filtrate, which was then acidulated with phosphoric acid and a little sulphuric. The liberated iodine was then titrated with sodium thiosulphate solution, which had been standardized by means of pure iodine, prepared by Stas' method. From the iodine thus measured the excessive oxygen was computed, and from that datum the atomic weight of chromium was found. For present purposes, however, the data may be used more directly, as giving the ratios I<sub>3</sub> : Ag<sub>2</sub>CrO<sub>4</sub> and I<sub>3</sub> : Ag<sub>2</sub>CrO<sub>4</sub>.4NH<sub>3</sub>. Thus treated, the weights are as follows, reduced to a vacuum. Reckoning the salt as 100, the third column gives the percentage of iodine liberated:

<i>Ag<sub>2</sub>CrO<sub>4</sub>.</i>	<i>I Set Free.</i>	<i>Percentage.</i>
.43838	.50251	114.628
.90258	1.03432	114.595
.89858	1.02980	114.603
.89868	1.03072	114.693
		<hr/>

$$\text{Mean, } 114.630, \pm .015$$

The next series, obviously, gives the ratio  $I_3 : Ag_2CrO_4.4NH_3$ .

$Ag_2CrO_4.4NH_3$ .	<i>I Set Free.</i>	<i>Percentage.*</i>
.54356	.51784	95.267
.54856	.52046	94.877
.54926	.52322	95.258
.54906	.52376	95.392
.54466	.51910	95.307
.54536	.51891	95.150

Mean, 95.208,  $\pm .0497$

In dealing with the two dichromates Meineke used the acid potassium iodate in place of potassium iodide, the chromate and the iodate reacting in the molecular ratio of 2 : 1. The thiosulphate was standardized by means of the acid iodate, so that we have direct ratios between the latter and the two chromates. The data are as follows, with the amount of iodate proportional to one hundred parts of the dichromate in the third column :

$K_2Cr_2O_7$ .	$KHI_2O_6$ .	<i>Percentage.</i>
.25090	.16609	66.198
.25095	.16613	66.200
.25078	.16601	66.197
.24979	.16541	66.220
.24987	.16540	66.192
.24966	.16543	66.262
.25015	.16559	66.196
.25012	.16559	66.204
.24977	.16546	66.245
.25034	.16572	66.198
.25025	.16567	66.202
.25015	.16568	66.234

Mean, 66.212,  $\pm .0044$

$Am_2Cr_2O_7$ .	$KHI_2O_6$ .	<i>Percentage.</i>
.21457	.16584	77.290
.21465	.16588	77.279
.21464	.16584	77.264
.21416	.16543	77.246
.21447	.16564	77.232
.21427	.16559	77.281
.22196	.17152	77.272
.22194	.17151	77.278
.22180	.17139	77.272

Mean, 77.268,  $\pm .0041$

\* These figures are not wholly in accord with the percentages of oxygen computed by Meineke. I suspect that there is a misprint among his data as published, probably in the second experiment, but I cannot trace it with certainty.

The following ratios are now available for computing the atomic weight of chromium :

- (1.) Percentage  $\text{Cr}_2\text{O}_3$  from  $\text{Ag}_2\text{CrO}_4$ , 22.934,  $\pm .0018$
- (2.) Percentage  $\text{Cr}_2\text{O}_3$  from  $\text{Ag}_2\text{Cr}_2\text{O}_7$ , 35.236,  $\pm .0335$
- (3.)  $2\text{AgCl} : \text{Ag}_2\text{CrO}_4 :: 100 : 115.760$ ,  $\pm .0069$
- (4.)  $2\text{AgCl} : \text{Ag}_2\text{Cr}_2\text{O}_7 :: 100 : 150.816$ ,  $\pm .074$
- (5.)  $4\text{AgCl} : \text{Cr}_2\text{O}_3 :: 100 : 26.620$ ,  $\pm .0052$
- (6.) Percentage  $\text{Cr}_2\text{O}_3$  in  $\text{Cr}_2(\text{SO}_4)_3$ , 38.838,  $\pm .0087$
- (7.) Percentage  $\text{Cr}_2\text{O}_3$  in  $\text{AmCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , 16.143,  $\pm .0125$
- (8.)  $\text{BaSO}_4 : \text{BaCrO}_4 :: 100 : 108.9815$ ,  $\pm .0369$
- (9.)  $\text{BaCrO}_4 : \text{BaCl}_2 :: 100 : 81.702$ ,  $\pm .014$
- (10.)  $3\text{AgCl} : \text{CrCl}_3 :: 100 : 36.842$ ,  $\pm .0031$
- (11.)  $2\text{KClO}_3 : \text{K}_2\text{Cr}_2\text{O}_7 :: 100 : 120.216$ ,  $\pm .0235$
- (12.) Percentage  $\text{Cr}_2\text{O}_3$  in  $\text{Ag}_2\text{CrO}_4 \cdot 4\text{NH}_3$ , 19.059,  $\pm .0074$
- (13.)  $2\text{AgCl} : \text{Ag}_2\text{CrO}_4 \cdot 4\text{NH}_3 :: 100 : 139.357$ ,  $\pm .1109$
- (14.) Percentage  $\text{Cr}_2\text{O}_3$  in  $\text{Am}_2\text{Cr}_2\text{O}_7$ , 60.337,  $\pm .0029$
- (15.)  $\text{Ag}_2\text{CrO}_4 : 3\text{I} :: 100 : 114.630$ ,  $\pm .015$
- (16.)  $\text{Ag}_2\text{CrO}_4 \cdot 4\text{NH}_3 : 3\text{I} :: 100 : 95.208$ ,  $\pm .0497$
- (17.)  $2\text{K}_2\text{Cr}_2\text{O}_7 : \text{KHI}_2\text{O}_6 :: 100 : 66.212$ ,  $\pm .0044$
- (18.)  $2\text{Am}_2\text{Cr}_2\text{O}_7 : \text{KHI}_2\text{O}_6 :: 100 : 77.268$ ,  $\pm .0041$

The antecedent values to use in the reduction are—

O = 15.879, $\pm .0003$	S = 31.828, $\pm .0015$
Ag = 107.108, $\pm .0031$	N = 13.935, $\pm .0021$
Cl = 35.179, $\pm .0048$	Ba = 136.392, $\pm .0086$
I = 125.888, $\pm .0069$	AgCl = 142.287, $\pm .0037$
K = 38.817, $\pm .0051$	

For the molecular weight of  $\text{Cr}_2\text{O}_3$ , seven values are now calculable, as follows :

From (1) .....	$\text{Cr}_2\text{O}_3 = 151.120$ , $\pm .0130$
From (2) .....	" = 151.105, $\pm .1636$
From (5) .....	" = 151.507, $\pm .0299$
From (6) .....	" = 151.384, $\pm .0341$
From (7) .....	" = 153.756, $\pm .1205$
From (12) .....	" = 151.478, $\pm .0606$
From (14) .....	" = 151.190, $\pm .0110$
General mean .....	$\text{Cr}_2\text{O}_3 = 151.229$ , $\pm .0039$

For silver chromate there are two values—

From (3) .....	$\text{Ag}_2\text{CrO}_4 = 329.423$ , $\pm .0195$
From (15) .....	" = 329.464, $\pm .0467$
General mean .....	$\text{Ag}_2\text{CrO}_4 = 329.430$ , $\pm .0180$

And for the ammonio-chromate we have—

From (13) .....	$\text{Ag}_2\text{CrO}_4 \cdot 4\text{NH}_3 = 396.574$ , $\pm .3158$
From (16) .....	" = 396.673, $\pm .2082$
General mean .....	$\text{Ag}_2\text{CrO}_4 \cdot 4\text{NH}_3 = 396.647$ , $\pm .1738$

From (4) .....	$\text{Ag}_2\text{Cr}_2\text{O}_7 = 429.177, \pm .2109$
From (10) .....	$\text{CrCl}_3 = 157.266, \pm .0113$
From (18) ... ..	$\text{Am}_2\text{Cr}_2\text{O}_7 = 250.341, \pm .0164$

For the molecular weights of  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{BaCrO}_4$  there are two estimates each, as given below :

From (11) .....	$\text{K}_2\text{Cr}_2\text{O}_7 = 292.433, \pm .0189$
From (17) .....	" $= 292.143, \pm .0224$
General mean .....	$\text{K}_2\text{Cr}_2\text{O}_7 = 292.311, \pm .0144$
From (8) .....	$\text{BaCrO}_4 = 252.549, \pm .0966$
From (9) .....	" $= 253.054, \pm .0377$
General mean .....	$\text{BaCrO}_4 = 252.985, \pm .0351$

Finally, from these molecular weights, eight independent values are obtained for the atomic weight of chromium :

From $\text{Cr}_2\text{O}_3$ .....	$\text{Cr} = 51.796, \pm .0039$
From $\text{Ag}_2\text{CrO}_4$ .....	" $= 51.698, \pm .0191$
From $\text{Ag}_2\text{CrO}_4, 4\text{NH}_3$ .....	" $= 51.175, \pm .1741$
From $\text{Ag}_2\text{Cr}_2\text{O}_7$ .....	" $= 51.904, \pm .1055$
From $\text{Am}_2\text{Cr}_2\text{O}_7$ .....	" $= 51.659, \pm .0085$
From $\text{K}_2\text{Cr}_2\text{O}_7$ .....	" $= 51.762, \pm .0102$
From $\text{CrCl}_3$ .....	" $= 51.729, \pm .0183$
From $\text{BaCrO}_4$ .....	" $= 53.077, \pm .0362$
General mean .....	$\text{Cr} = 51.778, \pm .0032$

If  $\text{O} = 16$ ,  $\text{Cr} = 52.172$ .

Rejecting the last of the eight values, that from barium chromate, the mean becomes—

$$\text{Cr} = 51.767, \pm .0032.$$

Even this result is probably too high, for it includes ratios which are certainly erroneous, and which yet exert appreciable weight. From the ratios which are reasonably concordant a better mean is derivable, as follows :

From (1) .....	$\text{Cr} = 51.741, \pm .0065$
From (2) .....	" $= 51.734, \pm .0818$
From (14) .....	" $= 51.776, \pm .0055$
From (3) and (15) .....	" $= 51.698, \pm .0191$
From (4) .....	" $= 51.904, \pm .1055$
From (10) .....	" $= 51.729, \pm .0183$
From (18) .....	" $= 51.659, \pm .0085$
From (11) and (17) .....	" $= 51.762, \pm .0102$
General mean .....	$\text{Cr} = 51.742, \pm .0034$

If  $\text{O} = 16$ , this becomes 52.136, a value which is probably not very far from the truth.

## MOLYBDENUM.

If we leave out of account the inaccurate determination made by Berzelius,\* we shall find that the data for the atomic weight of molybdenum lead to two independent estimates of its value—one near 92, the other near 96. The earlier results found by Berlin and by Svanberg and Struve lead to the lower number; the more recent investigations, together with considerations based upon the periodic law, point conclusively to the higher.

The earliest investigation which we need especially to consider is that of Svanberg and Struve.† These chemists tried a variety of different methods, but finally based their conclusions upon the two following: First, molybdenum trioxide was fused with potassium carbonate, and the carbon dioxide which was expelled was estimated; secondly, molybdenum disulphide was converted into the trioxide by roasting, and the ratio between the weights of the two substances was determined.

By the first method it was found that 100 parts of  $\text{MoO}_3$  will expel the following quantities of  $\text{CO}_2$ :

31.4954

31.3749

31.4705Mean, 31.4469,  $\pm .0248$ 

The carbon dioxide was determined simply from the loss of weight when the weighed quantities of trioxide and carbonate were fused together. It is plain that if, under these circumstances, a little of the trioxide should be volatilized, the total loss of weight would be slightly increased. A constant error of this kind would tend to bring out the atomic weight of molybdenum too low.

By the second method, the conversion by roasting of  $\text{MoS}_2$  into  $\text{MoO}_3$ , Svanberg and Struve obtained these results. Two samples of artificial disulphide were taken, A and B, and yielded for each hundred parts the following of trioxide:

$$\begin{array}{l} 89.7919 \\ 89.7291 \end{array} \left. \vphantom{\begin{array}{l} 89.7919 \\ 89.7291 \end{array}} \right\} \text{A.}$$

$$\begin{array}{l} 89.6436 \\ 89.7082 \\ 89.7660 \\ 89.7640 \\ 89.8635 \end{array} \left. \vphantom{\begin{array}{l} 89.6436 \\ 89.7082 \\ 89.7660 \\ 89.7640 \\ 89.8635 \end{array}} \right\} \text{B.}$$
Mean, 89.7523,  $\pm .0176$ 

Three other experiments in series B gave divergent results, and, although published, are rejected by the authors themselves. Hence it is

\* Poggend. Annalen, 8, 1. 1826

† Journ. für Prakt. Chem., 44, 301. 1848.

not necessary to cite them in this discussion. We again encounter in these figures the same source of constant error which apparently vitiates the preceding series, namely, the possible volatilization of the trioxide. Here, also, such an error would tend to reduce the atomic weight of molybdenum.

From the  $\text{CO}_2$  series .....  $\text{Mo} = 91.25$

From the  $\text{MoS}_2$  series. ....  $\text{Mo} = 92.49$

Berlin,\* a little later than Svanberg and Struve, determined the atomic weight of molybdenum by igniting a molybdate of ammonium and weighing the residual  $\text{MoO}_3$ . Here, again, a loss of the latter by volatilization may (and probably does) lead to too low a result. The salt used was  $(\text{NH}_4)_4\text{Mo}_5\text{O}_{17} \cdot 3\text{H}_2\text{O}$ , and in it these percentages of  $\text{MoO}_3$  were found :

81.598

81.612

81.558

81.555

Mean, 81.581,  $\pm .0095$

Hence  $\text{Mo} = 91.559$ .

Until 1859 the value 92 was generally accepted on the basis of the foregoing researches, but in this year Dumas† published some figures tending to sustain a higher number. He prepared molybdenum trioxide by roasting the disulphide, and then reduced it to metal by ignition in hydrogen. At the beginning the hydrogen was allowed to act at a comparatively low temperature, in order to avoid volatilization of trioxide; but at the end of the operation the heat was raised sufficiently to insure a complete reduction. From the weighings I calculate the percentages of metal in  $\text{MoO}_3$  :

.448	gram.	$\text{MoO}_3$	gave	.299	gram.	Mo.	66.741	per cent.
.484	"			.323	"		66.736	"
.484	"			.322	"		66.529	"
.498	"			.332	"		66.667	"
.559	"			.373	"		66.726	"
.388	"			.258	"		66.495	"

Mean, 66.649,  $\pm .030$

In 1868 the same method was employed by Debray.‡ His trioxide was purified by sublimation in a platinum tube. His percentages are as follows :

5.514	gram.	$\text{MoO}_3$	gave	3.667	gram.	Mo.	66.503	per cent.
7.910	"			5.265	"		61.561	"
9.031	"			6.015	"		66.604	"

Mean, 66.556,  $\pm .020$

\* Journ. für Prakt. Chem., 49, 444. 1850.

† Ann. Chem. Pharm., 105, 84, and 113, 23.

‡ Compt. Rend., 66, 734.

For the same ratio we have also a single experiment by Rammelsberg,\* who, closely following Dumas' method, found in molybdenum trioxide 66.708 per cent. of metal. As this figure falls within the limits of Dumas' series, we may assign it equal weight with one experiment in the latter.

Debray also made two experiments upon the precipitation of molybdenum trioxide in ammoniacal solution by nitrate of silver. In his results, as published, there is curious discrepancy, which, I have no doubt, is due to a typographical error. These results I am therefore compelled to leave out of consideration. They could not, however, exert a very profound influence upon the final discussion.

In 1873, Lothar Meyer† discussed the analyses made by Liechti and Kemp‡ of four chlorides of molybdenum, and in the former edition of this work the same data were considered in detail. The analyses, however, were not intended as determinations of atomic weight, and since good determinations have been more recently published, the work on the chlorides will be omitted from further consideration. It is enough to state here that they gave values for Mo ranging near 96, both above and below that number, with an extreme range of over eight-tenths of a unit.

In 1893 the determinations by Smith and Maas appeared,§ representing an entirely new method. Sodium molybdate, purified by many recrystallizations and afterwards dehydrated, was heated in a current of pure, dry, gaseous hydrochloric acid. The compound  $\text{MoO}_3 \cdot 2\text{HCl}$  was thus distilled off, and the sodium molybdate was quantitatively transformed into sodium chloride. The latter salt was afterwards carefully examined, and proved to be free from molybdenum. The data, with all weights reduced to a vacuum standard, are subjoined:

$\text{Na}_2\text{MoO}_4$ .	$\text{NaCl}$ .	Per cent. $\text{NaCl}$ .
1.14726	.65087	56.733
.89920	.51023	56.743
.70534	.40020	56.739
.70793	.40182	56.760
1.26347	.71695	56.745
1.15217	.65367	56.734
.90199	.51188	56.750
.81692	.46358	56.747
.65098	.36942	56.748
.80563	.45717	56.747

Mean, 56.745,  $\pm .0017$

In 1895, Seubert and Pollard|| determined the atomic weight of mo-

\* Berlin Monatsbericht, 1877, p. 574.

† Ann. Chem. Pharm., 169, 365. 1873.

‡ Ann. Chem. Pharm., 169, 344.

§ Journ. Amer. Chem. Soc., 15, 397. 1893.

|| Zeitsch. Anorg. Chem., 8, 434. 1895.



lybdenum by two methods. First, the carefully purified trioxide, in weighed amounts, was dissolved in an excess of a standard solution of caustic soda. This solution was standardized by means of hydrochloric acid, which in turn had been standardized gravimetrically as silver chloride. Hence, indirectly, the ratio  $2\text{AgCl} : \text{MoO}_3$  was measured. Sulphuric acid and lime water were also used in the titrations, so that the entire process was rather complicated. Ignoring the intermediate data, the end results, in weights of  $\text{MoO}_3$  and  $\text{AgCl}$ , were as follows. The third column gives the  $\text{MoO}_3$  proportional to 100 parts of  $\text{AgCl}$ :

<i>MoO<sub>3</sub>.</i>	<i>AgCl.</i>	<i>Ratio.</i>
3.6002	7.1709	50.206
3.5925	7.1569	50.196
3.7311	7.4304	50.214
3.8668	7.7011	50.211
3.9361	7.8407	50.201
3.8986	7.7649	50.208
3.9630	7.8941	50.202
3.9554	7.8806	50.192
3.9147	7.7999	50.189
3.8543	7.6767	50.208
3.9367	7.8437	50.190
		Mean, 50.202, $\pm .0018$

The second method adopted by Seubert and Pollard was the old one of reducing the trioxide to metal by heating in a current of hydrogen. The weights and percentages of metal are subjoined:

<i>MoO<sub>3</sub>.</i>	<i>Mo.</i>	<i>Per cent.</i>
1.8033	1.2021	66.661
1.9345	1.1564	66.670
3.9413	2.6275	66.666
1.5241	1.0160	66.662
4.0533	2.7027	66.679
		Mean, 66.668, $\pm .0022$

This mean may be combined with the results of previous investigators, thus:

Dumas . . . . .	66.649, $\pm .0300$
Debray . . . . .	66.556, $\pm .0200$
Rammelsberg . . . . .	66.708, $\pm .0680$
Seubert and Pollard . . . . .	66.668, $\pm .0022$
General mean . . . . .	66.665, $\pm .0022$

Here the data of Seubert and Pollard alone exert any appreciable influence.

Neglecting all determinations made previous to 1859, there are now

three ratios from which to compute the atomic weight of molybdenum, viz :

- (1.) Percentage Mo in  $\text{MoO}_3$ , 66.665,  $\pm .0022$ .
- (2.)  $2\text{AgCl} : \text{MoO}_3 :: 100 : 50.202$ ,  $\pm .0018$
- (3.)  $2\text{NaCl} : \text{Ma}_2\text{MoO}_4 : 56.745$ ,  $\pm .0017 : 100$ .

These involve the following values :

$\text{O} = 15.879$ , $\pm .0003$	$\text{AgCl} = 142.287$ , $\pm .0037$
$\text{Na} = 22.881$ , $\pm .0046$	$\text{NaCl} = 58.060$ , $\pm .0017$

Hence for the atomic weight in question—

From (1) .....	$\text{Mo} = 95.267$ , $\pm .0072$
From (2) .....	" = $95.225$ , $\pm .0064$
From (3) .....	" = $95.357$ , $\pm .0126$
General mean.....	$\text{Mo} = 95.259$ , $\pm .0045$

With  $\text{O} = 16$ ,  $\text{Mo} = 95.985$ .

This value is essentially that derived from Seubert and Pollard's data alone. Reducing the latter to a vacuum would affect the result very slightly—so slightly that the correction may be ignored.

## TUNGSTEN.

The atomic weight of tungsten has been determined from analyses of the trioxide, the hexachloride, and the tungstates of iron, silver, and barium.

The composition of the trioxide has been the subject of many investigations. Malaguti\* reduced this substance to the blue oxide, and from the difference between the weights of the two compounds obtained a result now known to be considerably too high. In general, however, the method of investigation has been to reduce  $\text{WO}_3$  to W in a stream of hydrogen at a white heat, and afterwards to reoxidize the metal, thus getting from one sample of material two results for the percentage of tungsten. This method is probably accurate, provided that the trioxide used be pure.

The first experiments which we need consider are, as usual, those of Berzelius.† 899 parts  $\text{WO}_3$  gave, on reduction, 716 of metal. 676 of metal, reoxidized, gave 846  $\text{WO}_3$ . Hence these percentages of W in  $\text{WO}_3$ :

$$\begin{array}{r} 79.644, \text{ by reduction.} \\ 79.905, \text{ by oxidation.} \\ \hline \end{array}$$

$$\text{Mean, } 79.7745, \pm .0880$$

These figures are far too high, the error being undoubtedly due to the presence of alkaline impurity in the trioxide employed.

Next in order of time comes the work of Schneider,‡ who with characteristic carefulness, took every precaution to get pure material. His percentages of tungsten are as follows:

*Reduction Series.*

$$\begin{array}{r} 79.336 \\ 79.254 \\ 79.312 \\ 79.326 \\ 79.350 \\ \hline \end{array}$$

$$\text{Mean, } 79.3156$$

*Oxidation Series.*

$$\begin{array}{r} 79.329 \\ 79.324 \\ 79.328 \\ \hline \end{array}$$

$$\text{Mean, } 79.327$$

$$\text{Mean of all, } 79.320, \pm .0068$$

\* Journ. für Prakt. Chem., 8, 179. 1836.

† Poggend. Annalen, 8, 1. 1825.

‡ Journ. für Prakt. Chem., 50, 152. 1850.

Closely agreeing with these figures are those of Marchand,\* published in the following year :

*Reduction Series.*

79.307

79.302

Mean, 79.3045

*Oxidation Series.*

79.321

79.352

Mean, 79.3365

Mean of all, 79.3205,  $\pm .0073$

The figures obtained by v. Borch † agree in mean tolerably well with the foregoing. They are as follows :

*Reduction Series.*

79.310

79.212

79.289

79.313

79.225

79.290

79.302

Mean, 79.277

*Oxidation Series.*

79.359

79.339

Mean, 79.349

Mean of all, 79.293,  $\pm .0108$

Dumas ‡ gives only a reduction series, based upon trioxide obtained by the ignition of a pure ammonium tungstate. The reduction was effected in a porcelain boat, platinum being objectionable on account of the tendency of tungsten to alloy with it. Dumas publishes only weighings, from which I have calculated the percentages :

2.784	gram.	WO <sub>3</sub>	gave	2.208	gram.	W.	79.310	per cent.
2.994	“	“	“	2.373	“	“	79.259	“
4.600	“	“	“	3.649	“	“	79.326	“
.985	“	“	“	.781	“	“	79.289	“
.917	“	“	“	.727	“	“	79.280	“
.917	“	“	“	.728	“	“	79.389	“
1.717	“	“	“	1.362	“	“	79.324	“
2.988	“	“	“	2.370	“	“	79.317	“

Mean, 79.312,  $\pm .009$

\* Ann. Chem. Pharm., 77, 261. 1851.

† Journ. für Prakt. Chem., 54, 254. 1851.

‡ Ann. Chem. Pharm., 113, 23. 1860.

The data furnished by Bernoulli\* differ widely from those just given. This chemist undoubtedly worked with impure material, the trioxide having a greenish tinge. Hence the results are too high. These are the percentages of W :

*Reduction Series.*

79.556  
79.526  
79.553  
79.558  
79.549  
78.736

Mean, 79.413

*Oxidation Series.*

79.558  
79.656  
79.555  
79.554

Mean, 79.581

Mean of all, 79.480,  $\pm .056$

Two reduction experiments by Persoz† give the following results :

1.7999 gm. $WO_3$	gave 1.4274 gm. W.	79.304 per cent.
2.249	" 1.784 "	<u>79.324</u> "
		Mean, 79.314, $\pm .007$

Next in order is the work done by Roscoe.‡ This chemist used a porcelain boat and tube, and made six weighings, after successive reductions and oxidations, with the same sample of 7.884 grammes of trioxide. These weighings give me the following five percentages, which, for the sake of uniformity with foregoing series, I have classified under the usual, separate headings :

*Reduction Series.*

79.196  
79.285  
79.308

Mean, 79.263

*Oxidation Series.*

79.230  
79.299

Mean, 79.2645

Mean of all, 79.264,  $\pm .0146$

\* Poggend. Annalen, 111, 573. 1860.

† Zeit. Anal. Chem., 3, 260. 1864.

‡ Ann. Chem. Pharm., 162, 368. 1872.

In Waddell's experiments\* especial precautions were taken to procure tungstic oxide free from silica and molybdenum. Such oxide, elaborately purified, was reduced in hydrogen, with the following results :

1.4006	gram. $\text{WO}_3$ gave	1.1115	W.	79.359	per cent.
.9900	"	.7855	"	79.343	"
1.1479	"	.9110	"	79.362	"
.9894	"	.7847	"	79.311	"
4.5639	"	3.6201	"	79.320	"
				<hr/>	
				79.339,	$\pm .0069$

The investigation by Pennington and Smith† started from the supposition that the tungsten compounds studied by their predecessors had not been completely freed from molybdenum. Accordingly, tungstic oxide, carefully freed from all other impurities, was heated in a stream of gaseous hydrochloric acid, so as to volatilize all molybdenum as the compound  $\text{MoO}_3 \cdot 2\text{HCl}$ . The residual  $\text{WO}_3$  was then reduced in pure hydrogen, and the tungsten so obtained was oxidized in porcelain crucibles. Care was taken to exclude reducing gases, and the trioxide was finally cooled in vacuum desiccators over sulphuric acid. The oxidation data are as follows, with the usual percentage column added. The weights are reduced to a vacuum :

<i>Tungsten.</i>	<i>Oxygen Gained.</i>	<i>Percentage.</i>
.862871	.223952	79.394
.650700	.168900	79.392
.597654	.155143	79.390
.666820	.173103	79.391
.428228	.111168	79.390
.671920	.174406	79.392
.590220	.153193	79.394
.568654	.147588	79.394
1.080973	.280600	79.392
		<hr/>

Mean, 79.392,  $\pm .0004$

With  $\text{O} = 16$ , this series gives  $\text{W} = 184.92$ .

The very high value for tungsten found by Pennington and Smith, nearly a unit higher than that which was commonly accepted, seems to have at once attracted the attention of Schneider,‡ who criticised the paper somewhat fully, and gave some new determinations of his own. The tungsten trioxide employed in this new investigation was heated in gaseous hydrochloric acid, and the absence of molybdenum was proved. The data obtained, both by reduction and by oxidation, are as follows :

\* Am. Chem. Journ., 8, 280. 1886.

† Read before the Amer. Philos. Soc., Nov. 2, 1894.

‡ Journ. für Prakt. Chem. (2), 53, 288. 1896.

*Reduction Series.*

2.0738	gram. $\text{WO}_3$ gave	1.6450	W.	79.323	per cent.
4.0853	"	3.2400	"	79.309	"
6.1547	"	4.8811	"	79.307	"

*Oxidation Series.*

1.5253	gram. W gave	1.9232	$\text{WO}_3$ .	79.311	per cent.
3.1938	"	4.0273	"	79.304	"
4.7468	"	5.9848	"	79.314	"

Mean of all, 79.311,  $\pm .0018$

Hence with  $\text{O} = 16$ ,  $\text{W} = 184.007$ .

In order to account for the difference between this result and that of Pennington and Smith, an impurity of molybdenum trioxide amounting to about one per cent. would be necessary. Schneider suggests that the quantities of material used by Pennington and Smith were too small, and that there may have been mechanical loss of small particles during the long heatings. Such losses would tend to raise the atomic weight computed from the experiments. On the other hand, the losses could hardly have been uniform in extent, and the extremely low probable error of Pennington and Smith's series renders Schneider's supposition improbable. The error, if error exists, must be accounted for otherwise.

Since Schneider's paper appeared, another set of determinations by Shinn\* has been published from Smith's laboratory. Attempts to verify the results obtained by Smith and Desi having proved abortive, and other experiments having failed, Shinn resorted to the oxidation method and gives the subjoined data. The percentage column is added by myself:

.22297	gram. W gave	.28090	$\text{WO}_3$ .	79.377
.17200	"	.21664	"	79.394
.10989	"	.13844	"	79.377
.10005	"	.12598	"	79.417

Mean, 79.391,  $\pm .0066$

This figure is very close to that found in Pennington and Smith's series, and therefore serves as a confirmation. The discordance between these results and Schneider's is still to be explained.

There are still other experiments by Riche,† which I have not been able to get in detail. They cannot be of any value, however, for they give to tungsten an atomic weight of about ten units too low. We may therefore neglect this series, and go on to combine the others:

Berzelius	79.7745, $\pm .0880$
Schneider, 1850	79.320, $\pm .0068$
Marchand	79.3205, $\pm .0073$
v. Borch	79.293, $\pm .0108$
Dumas	79.312, $\pm .0090$

\* Doctoral thesis., University of Pennsylvania, 1896. "The atomic mass of tungsten."

† Journ. für Prakt. Chem., 69, 10. 1857.

Bernoulli.....	79.480, ± .0560
Persoz.....	79.314, ± .0070
Roscoe.....	79.264, ± .0146
Waddell.....	79.339, ± .0069
Pennington and Smith.....	79.392, ± .0004
Schneider, 1896.....	79.311, ± .0018
Shinn.....	79.391, ± .0066
General mean .....	79.388, ± .00039

Here the work of Pennington and Smith vastly outweighs everything else; and if their supposition as to the presence of molybdenum in all the previous investigations is correct, this result is to be accepted.

The rejection of the figures given by Berzelius and by Bernoulli would exert an unimportant influence upon the final result. There is, therefore, no practical objection to retaining them in the discussion.

In 1861 Scheibler\* deduced the atomic weight of tungsten from analyses of barium metatungstate,  $\text{BaO} \cdot 4\text{WO}_3 \cdot 9\text{H}_2\text{O}$ . In four experiments he estimated the barium as sulphate, getting closely concordant results, which were, however, very far too low. These, therefore, are rejected. But from the percentage of water in the salt a better result was attained. The percentages of water are as follows:

13.053
13.054
13.045
13.010
13.022

Mean, 13.0368, ± .0060

The work of Zettnow,† published in 1867, was somewhat more complicated than any of the foregoing researches. He prepared the pure tungstates of silver and of iron, and from their composition determined the atomic weight of tungsten.

In the case of the iron salt the method of working was this: The pure, artificial  $\text{FeWO}_4$  was fused with sodium carbonate, the resulting sodium tungstate was extracted by water, and the thoroughly washed, residual ferric oxide was dissolved in hydrochloric acid. This solution was then reduced by zinc, and titrated for iron with potassium permanganate. Corrections were applied for the drop in excess of permanganate needed to produce distinct reddening, and for the iron contained in the zinc. 11.956 grammes of the latter metal contained iron corresponding to 0.6 cc. of the standard solution. The permanganate was standardized by comparison with pure ammonium-ferrous sulphate,  $\text{Am}_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , so that, in point of fact, Zettnow establishes directly only the ratio between that salt and the ferrous tungstate. From Zettnow's four experiments in standardizing I find that 1 cc. of his solution

\* Journ. für Prakt. Chem., 83, 324.

† Poggend. Annalen, 130, 30.



corresponds to 0.0365457 gramme of the double sulphate, with a probable error of  $\pm .0000012$ .

Three sets of titrations were made. In the first a quantity of ferrous tungstate was treated according to the process given above; the iron solution was diluted to 500 cc., and four titrations made upon 100 cc. at a time. The second set was like the first, except that three titrations were made with 100 cc. each, and a fourth upon 150 cc. In the third set the iron solution was diluted to 300 cc., and only two titrations upon 100 cc. each were made. In sets one and two thirty grammes of zinc were used for the reduction of each, while in number three but twenty grammes were taken. Zettnow's figures, as given by him, are quite complicated; therefore I have reduced them to a common standard. After applying all corrections the following quantities of tungstate, in grammes, correspond to 1 cc. of permanganate solution:

.028301	} First set.
.028291	
.028311	
.028301	} Second set.
.028367	
.028368	
.028367	
.028367	} Third set.
.028438	
.028438	

Mean, .0283549,  $\pm .0000115$

With the silver tungstate,  $\text{Ag}_2\text{WO}_4$ , Zettnow employed two methods. In two experiments the substance was decomposed by nitric acid, and the silver thus taken into solution was titrated with standard sodium chloride. In three others the tungstate was treated directly with common salt, and the residual silver chloride collected and weighed. Here again, on account of some complexity in Zettnow's figures, I am compelled to reduce his data to a common standard. To 100 parts of  $\text{AgCl}$  the following quantities of  $\text{Ag}_2\text{WO}_4$  correspond:

*By First Method.*

161.665  
161.603

Mean, 161.634,  $\pm .021$

*By Second Method.*

161.687  
161.651  
161.613

Mean, 161.650,  $\pm .014$

General mean from both series, 161.645,  $\pm .012$

For tungsten hexchloride we have two analyses by Roscoe, published in the same paper with his results upon the trioxide. In one experiment the chlorine was determined as AgCl; in the other the chloride was reduced by hydrogen, and the residual tungsten estimated. By bringing both results into one form of expression we have for the percentage of chlorine in  $WCl_6$ :\*

$$\begin{array}{r} 53.588 \\ 53.632 \\ \hline \text{Mean, } 53.610, \pm .015 \end{array}$$

The work done by Smith and Desi † probably ought to be considered in connection with that of Pennington and Smith on the trioxide. Smith and Desi started with tungsten trioxide, freed from molybdenum by means of gaseous hydrochloric acid. This material was reduced in a stream of carefully purified hydrogen, and the water formed was collected in a calcium chloride tube and weighed. To the results found I add the percentage of water obtained from 100 parts of  $WO_3$ . Vacuum weights are given.

$WO_3$ .	$H_2O$ .	Per cent. $H_2O$ .
.983024	.22834	23.228
.998424	.23189	23.226
1.008074	.23409	23.221
.911974	.21184	23.229
.997974	.23179	23.226
1.007024	.23389	23.226

$$\text{Mean, } 23.226, \pm .0008$$

There are now six ratios from which to calculate the atomic weight of tungsten :

- (1.) Percentage of W in  $WO_3$ , 79.388,  $\pm .00039$
- (2.) Percentage of  $H_2O$  in  $BaO \cdot 4WO_3 \cdot 9H_2O$ , 13.0368,  $\pm .0060$
- (3.)  $WO_3 : 3H_2O :: 100 : 23.226, \pm .0008$
- (4.)  $Am_2Fe(SO_4)_2 \cdot 6H_2O : FeWO_4 :: .0365457, \pm .0000012 : .0283549, \pm .0000115$
- (5.)  $2AgCl : Ag_2WO_4 :: 100 : 161.645, \pm .012$
- (6.) Percentage of Cl in  $WCl_6$ , 53.610,  $\pm .015$

These are reduced with—

O = 15.879, $\pm .0003$	S = 31.828, $\pm .0015$
Ag = 107.108, $\pm .0031$	Ba = 136.392, $\pm .0086$
Cl = 35.179, $\pm .0048$	Fe = 55.597, $\pm .0023$
N = 13.935, $\pm .0021$	AgCl = 142.287, $\pm .0037$

\* The actual figures are as follows :

19.5700 grm. $WCl_6$ gave 42.4127 grm. AgCl.
10.4326 " 4.8374 grm. tungsten.

† Read before Amer. Philos. Soc., Nov. 2, 1894.

Hence there are six values for the atomic weight of tungsten, as follows :

From (1) .....	W = 183.485, $\pm$ .0051
From (2) .....	" = 182.638, $\pm$ .1248
From (3) .....	" = 183.298, $\pm$ .0088
From (4) .....	" = 183.035, $\pm$ .1229
From (5) .....	" = 182.268, $\pm$ .0663
From (6) .....	" = 182.647, $\pm$ .0820
<hr/>	
General mean .....	W = 183.429, $\pm$ .0044

If O = 16, W = 184.827. The rejection of all values except the first and third raises the mean by 0.009; that is, four of the ratios count for almost nothing, and the work done in Smith's laboratory dominates all the rest. The questions raised by Schneider in his latest determination, however, are not yet answered, and farther investigation is required in order to fully establish the true atomic weight of tungsten.

## URANIUM.

The earlier attempts to determine the atomic weight of uranium were all vitiated by the erroneous supposition that the uranous oxide was really the metal. The supposition, of course, does not affect the weighings and analytical data which were obtained, although these, from their discordance with each other and with later and better results, have now only a historical value.

For present purposes the determinations made by Berzelius,\* by Arfvedson,† and by Marchand‡ may be left quite out of account. Berzelius employed various methods, while the others relied upon estimating the percentage of oxygen lost upon the reduction of  $U_3O_8$  to  $UO_2$ . Rammelsberg's§ results also, although very suggestive, need no full discussion. He analyzed the green chloride,  $UCl_4$ ; effected the synthesis of uranyl sulphate from uranous oxide; determined the amount of residue left upon the ignition of the sodio and bario-uranic acetates; estimated the quantity of magnesium uranate formed from a known weight of  $UO_2$ , and attempted also to fix the ratio between the green and the black oxides. His figures vary so widely that they could count for little in the establishing of any general mean; and, moreover, they lead to estimates of the atomic weight which are mostly below the true value. For instance, twelve lots of  $U_3O_8$  from several different sources were reduced to  $UO_2$  by heating in hydrogen. The percentages of loss varied from 3.83 to 4.67, the mean being 4.121. These figures give values for the atomic

\* Schweigg. Journ., 22, 336. 1818. Poggend. Annalen, 1, 359. 1825.

† Poggend. Annalen, 1, 245. Berz. Jahr., 3, 120. 1822.

‡ Journ. für Prakt. Chem., 23, 497. 1841.

§ Poggend. Annalen, 55, 318, 1842; 56, 125, 1842; 59, 9, 1843; 66, 91, 1845. Journ. für Prakt. Chem., 29, 324.

weight of uranium ranging from 184.33 to 234.05, or, in mean, 214.53. Such discordance is due partly to impurity in some of the material studied, and illustrates the difficulties inherent in the problem to be solved. Some of the uranoso-uranic oxide was prepared by calcining the oxalate, and retained an admixture of carbon. Many such points were worked up by Rammelsberg with much care, so that his papers should be scrupulously studied by any chemist who contemplates a redetermination of the atomic weight of uranium.

In 1841 and 1842 Peligot published certain papers\* showing that the atomic weight of uranium must be somewhere near 240. A few years later the same chemist published fuller data concerning the constant in question, but in the time intervening between his earlier and his final researches other determinations were made by Ebelmen and by Wertheim. These investigations we may properly discuss in chronological order. For present purposes the early work of Peligot may be dismissed as only preliminary in character. It showed that what had been previously regarded as metallic uranium was in reality an oxide, but gave figures for the atomic weight of the metal which were merely approximations.

Ebelmen's† determinations of the atomic weight of uranium were based upon analyses of uranic oxalate. This salt was dried at 100°, and then, in weighed amount, ignited in hydrogen. The residual uranous oxide was weighed, and in some cases converted into  $U_3O_8$  by heating in oxygen. The following weights are reduced to a vacuum standard:

10.1644	grm. oxalate gave	7.2939	grm. $UO_2$ .	
12.9985	"	9.3312	"	Gain on oxidation, .3685
11.8007	"	8.4690	"	" .3275
9.9923	"	7.1731	"	" .2812
11.0887	"	7.9610	"	" .3105
10.0830	"	7.2389	"	
6.7940	"	4.8766	"	
16.0594	"	11.5290	"	" .4531

Reducing these figures to percentages, we may present the results in two columns. Column A gives the percentages of  $UO_2$  in the oxalate, while B represents the amount of  $U_2O_3$  formed from 100 parts of  $UO_2$ :

A.	B.
71.924	.....
71.787	103.949
71.767	103.867
71.621	103.920
71.794	103.900
71.793	.....
71.778	.....
71.790	103.930
Mean, 71.782, $\pm .019$	Mean, 103.913, $\pm .009$

\* Compt. Rend., 12, 735. 1841. Ann. Chim. Phys. (3), 55. 1842.

† Journ. für Prakt. Chem., 27, 385. 1842.

Wertheim's\* experiments were even simpler in character than those of Ebelmen. Sodio-uranic acetate, carefully dried at 200°, was ignited, leaving the following percentages of sodium uranate :

67.51508
67.54558
67.50927
<hr/>
Mean, 67.52331, $\pm .0076$

The final results of Peligot's† investigations appeared in 1846. Both the oxalate and the acetate of uranium were studied and subjected to combustion analysis. The oxalate was scrupulously purified by repeated crystallizations, and thirteen analyses, representing different fractions, were made. Seven of these gave imperfect results, due to incomplete purification of the material; six only, from the later crystallizations, need to be considered. In these the uranium was weighed as  $U_3O_8$ , and the carbon as  $CO_2$ . From the ratio between the  $CO_2$  and  $U_3O_8$  the atomic weight of uranium may be calculated without involving any error due to traces of moisture possibly present in the oxalate. I subjoin Peligot's weighings, and give, in the third column, the  $U_3O_8$  proportional to 100 parts of  $CO_2$  :

$CO_2$ .	$U_3O_8$ .	Ratio.
1.456 gm.	4.649 gm.	319.299
1.369 "	4.412 "	322.279
2.209 "	7.084 "	320.688
1.019 "	3.279 "	321.786
1.069 "	3.447 "	322.461
1.052 "	3.389 "	322.148

Mean, 321.443, ± .338

From the acetate,  $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$ , the following percentages of  $U_3O_8$  were obtained :

5.061 gm. acetate gave	3.354 gm. $U_3O_8$ .	66.2715 per cent.
4.601 "	3.057 "	66.4421 "
1.869 "	1.238 "	66.2386 "
3.817 "	2.541 "	66.5706 "
10.182 "	6.757 "	66.3622 "
4.393 "	2.920 "	66.4694 "
2.868 "	1.897 "	66.1437 "

Mean, 66.3569, ± .038

The acetate also yielded the subjoined percentages of carbon and of water. Assuming that the figures for carbon were calculated from known

\* Journ. für Prakt. Chem., 29, 209. 1843.

† Compt. Rend., 22, 487. 1846.

weights of dioxide, with  $C = 12$  and  $O = 16$ , I have added a third column, in which the carbon percentages are converted into percentages of  $CO_2$ :

$H_2O$ .	$C$ .	$CO_2$ .
21.60	11.27	41.323
21.16	11.30	41.433
21.10	11.30	41.433
21.20	11.10	40.700
Mean, 21.265, $\pm .187$	Mean, 11.24	Mean, 41.222, $\pm .092$

From these data we get the following values for the molecular weight of uranyl acetate:

From percentage of $U_3O_8$ .....	423.183, $\pm .4781$
From percentage of $CO_2$ .....	423.842, $\pm .9462$
From percentage of $H_2O$ .....	420.386, $\pm 2.9033$
General mean .....	423.257, $\pm .4222$

In the posthumous paper of Zimmermann, edited by Krüss and Alibegoff,\* the atomic weight of uranium is determined by two methods. First,  $UO_2$ , prepared by several methods, is converted into  $U_3O_8$  by heating in oxygen. To begin with,  $U_3O_8$  was prepared, and reduced to  $UO_2$  by ignition in hydrogen. When the reduction takes place at moderate temperatures, the  $UO_2$  is somewhat pyrophoric, but if the operation is performed over the blast lamp this difficulty is avoided. After weighing the  $UO_2$ , the oxidation is effected, and the gain in weight observed. The preliminary  $U_3O_8$  was derived from the following sources: A, from uranium tetroxide; B, from the oxalate; C, from uranyl nitrate; D, by precipitation with mercuric oxide. The full data, lettered as indicated above, are subjoined:

	$UO_2$ .	$U_3O_8$ .	Per cent. of Gain.
A. {	8.9363	9.2872	3.927
	7.9659	8.2789	3.929
	12.4385	12.9270	3.927
B. {	12.8855	13.3913	3.925
	5.7089	5.9331	3.927
	9.6270	10.0051	3.928
C. {	13.1855	13.7036	3.929
	9.9973	10.3901	3.929
D. {	15.8996	16.5242	3.928
	7.4326	7.7245	3.927
Mean, 3.9276, $\pm .0003$			
Ebelmen found, 3.913, $\pm .009$			
General mean, 3.9276, $\pm .0003$			

In short, Ebelmen's mean vanishes when combined with Zimmermann's.

\* Ann. d. Chem., 232, 299. 1886.

Zimmermann's second method was essentially that of Wertheim, namely, the ignition of the double acetate  $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{NaC}_2\text{H}_3\text{O}_2$ , the residue being sodium uranate,  $\text{Na}_2\text{U}_2\text{O}_7$ .

<i>Double Acetate.</i>	<i>Uranate.</i>	<i>Per cent. Uranate.</i>	
4.272984	2.886696	67.557	•
5.272094	3.560770	67.540	
2.912283	1.967428	67.556	
3.181571	2.149309	67.555	
		Mean, 67.552, $\pm .0027$	
		Wertheim found, 67.523, $\pm .0076$	
		General mean, 67.549, $\pm .0025$	

All the data for uranium now sum up thus:

- (1.) Per cent.  $\text{UO}_2$  from uranyl oxalate, 71.782,  $\pm .019$
- (2.)  $6\text{CO}_2 : \text{U}_3\text{O}_8 :: 100 : 321.443$ ,  $\pm .338$
- (3.) Molecular weight of uranyl acetate, 423.842,  $\pm .4222$
- (4.)  $3\text{UO}_2 : \text{U}_3\text{O}_8 :: 100 : 103.9276$ ,  $\pm .0003$
- (5.) Per cent.  $\text{Na}_2\text{U}_2\text{O}_7$  from  $\text{UO}_2 \cdot \text{Na}(\text{C}_2\text{H}_3\text{O}_2)_3$ , 67.549,  $\pm .0025$

Computing with  $\text{O} = 15.879$ ,  $\pm .0003$ ;  $\text{C} = 11.920$ ,  $\pm .0004$ , and  $\text{Na} = 22.881$ ,  $\pm .0046$ , we have—

From (1).....	U = 235.948, $\pm .1938$
From (2).....	" = 238.462, $\pm .2953$
From (3).....	" = 238.541, $\pm .4223$
From (4).....	" = 237.770, $\pm .0055$
From (5).....	" = 237.902, $\pm .0283$
General mean .....	U = 237.774, $\pm .0054$

If  $\text{O} = 16$ ,  $\text{U} = 239.586$ .

In this case Zimmermann's data control the final result. All the other determinations might be rejected without appreciable effect.

## SELENIUM.

The atomic weight of this element was first determined by Berzelius,\* who, saturating 100 parts of selenium with chlorine, found that 179 of chloride were produced. Further on these figures will be combined with similar results by Dumas.

We may omit, as unimportant for present purposes, the analyses of alkaline selenates made by Mitscherlich and Nitzsch,† and pass on to the experiments published by Sacc‡ in 1847. This chemist resorted to a variety of methods, some of which gave good results, while others were unsatisfactory. First, he sought to establish the exact composition of  $\text{SeO}_2$ , both by synthesis and by analysis. The former plan, according to which he oxidized pure selenium by nitric acid, gave poor results; better figures were obtained upon reducing  $\text{SeO}_2$  with ammonium bisulphite and hydrochloric acid, and determining the percentage of selenium set free:

.6800	gram.	$\text{SeO}_2$	gave	.4828	gram.	Se.	71.000	per cent.
3.5227		"		2.5047		"	71.102	"
4.4870		"		3.1930		"	71.161	"

Mean, 71.088,  $\pm .032$

In a similar manner Sacc also reduced barium selenite, and weighed the resulting mixture of barium sulphate and free selenium. This process gave discordant results, and a better method was found in calcining  $\text{BaSeO}_3$  with sulphuric acid, and estimating the resulting quantity of  $\text{BaSO}_4$ . In the third column I give the amounts of  $\text{BaSO}_4$  equivalent to 100 of  $\text{BaSeO}_3$ :

.5573	gram.	$\text{BaSeO}_3$	gave	.4929	gram.	$\text{BaSO}_4$ .	88.444
.9942		"		.8797		"	88.383
.2351		"		.2080		"	88.473
.9747		"		.8621		"	88.448

Mean, 88.437,  $\pm .013$

Still other experiments were made with the selenites of silver and lead; but the figures were subject to such errors that they need no further discussion here.

A few years after Sacc's work was published, Erdmann and Marchand made with their usual care a series of experiments upon the atomic weight under consideration.§ They analyzed pure mercuric selenide, which had been repeatedly sublimed and was well crystallized. Their

\* Poggend. Annalen, 8, 1. 1826.

† Poggend. Annalen, 9, 623. 1827.

‡ Ann. d. Chim. et d. Phys. (3), 21, 119.

§ Jour. für Prakt. Chem., 55, 202. 1852.



method of manipulation has already been described in the chapter upon mercury. These percentages of Hg in HgSe were found :

71.726
71.731
71.741

Mean, 71.7327,  $\pm .003$

The next determinations were made by Dumas,\* who returned to the original method of Berzelius. Pure selenium was converted by dry chlorine into  $\text{SeCl}_4$ , and from the gain in weight the ratio between Se and Cl was easily deducible. I include Berzelius' single experiment, which I have already cited, and give in a third column the quantity of chlorine absorbed by 100 parts of selenium :

1.709	gm. Se absorb	3.049	gm. Cl.	178.409
1.810	"	3.219	"	177.845
1.679	"	3.003	"	178.856
1.498	"	2.688	"	179.439
1.944	"	3.468	"	178.395
1.887	"	3.382	"	179.226
1.935	"	3.452	"	178.398
				179.000—Berzelius.

Mean, 178.696,  $\pm .125$

The question may here be properly asked, whether it would be possible thus to form  $\text{SeCl}_4$ , and be certain of its absolute purity? A trace of oxychloride, if simultaneously formed, would increase the apparent atomic weight of selenium. In point of fact, this method gives a higher value for Se than any of the other processes which have been adopted, and that value has the largest probable error of any one in the entire series. A glance at the table which summarizes the discussion at the end of this chapter will render this point sufficiently clear.

Still later, Ekman and Pettersson † investigated several methods for the determination of this atomic weight, and finally decided upon the two following :

First, pure silver selenite,  $\text{Ag}_2\text{SeO}_3$ , was ignited, leaving behind metallic silver, which, however, sometimes retained minute traces of selenium. The data obtained were as follows :

$\text{Ag}_2\text{SeO}_3$ .	Ag.	Per cent. Ag.
5.2102	3.2787	62.93
5.9721	3.7597	62.95
7.2741	4.5803	62.97
7.5390	4.7450	62.94
6.9250	4.3612	62.98
7.3455	4.6260	62.98
6.9878	4.3992	62.95

Mean, 62.957,  $\pm .005$

\* Ann. Chem. Pharm., 113, 32. 1860.

† Ber. d. Deutsch. Chem. Gesell., 9, 1210. 1876. Published in detail by the society at Upsala.

Secondly, a warm aqueous solution of selenious acid was mixed with HCl, and reduced by a current of  $\text{SO}_2$ . The reduced Se was collected upon a glass filter, dried, and weighed.

<i>SeO<sub>2</sub></i>	<i>Se.</i>	<i>Per cent. Se.</i>
11.1760	7.9573	71.199
11.2453	8.0053	71.185
24.4729	17.4232	71.193
20.8444	14.8383	71.187
31.6913	22.5600	71.191
		<hr/>
		Mean, 71.191, $\pm .0016$
..		Sacc found, 71.088, $\pm .0320$
		<hr/>
		General mean, 71.1907, $\pm .0016$

There are now five series of figures from which to deduce the atomic weight of selenium :

- (1.) Per cent. of Se in  $\text{SeO}_2$ , 71.1907,  $\pm .0016$
- (2.)  $\text{BaSeO}_3 : \text{BaSO}_4 :: 100 : 88.437$ ,  $\pm .013$
- (3.) Per cent. of Hg in  $\text{HgSe}$ , 71.7327,  $\pm .003$
- (4.)  $\text{Se} : \text{Cl}_4 :: 100 : 178.696$ ,  $\pm .125$
- (5.) Per cent. of Ag in  $\text{Ag}_2\text{SeO}_3$ , 62.957,  $\pm .005$

From these, computing with—

O = 15.879, $\pm .0003$	S = 31.828, $\pm .0015$
Ag = 107.108, $\pm .0031$	Ba = 136.392, $\pm .0086$
Cl = 35.179, $\pm .0048$	Hg = 198.491, $\pm .0083$ ,

five values for Se are calculable, as follows :

From (1).....	Se = 78.477, $\pm .0049$
From (2).....	" = 78.006, $\pm .0410$
From (3). .....	" = 78.217, $\pm .0095$
From (4).....	" = 78.740, $\pm .0561$
From (5).....	" = 78.405, $\pm .0201$
<hr/>	
General mean.....	Se = 78.419, $\pm .0042$

If O = 16, this becomes Se = 79.016.

## TELLURIUM.

Particular interest attaches to the atomic weight of tellurium on account of its relations to the periodic law. According to that law, tellurium should lie between antimony and iodine, having an atomic weight greater than 120 and less than 126. Theoretically, Mendelejeff assigns it a value of  $\text{Te} = 125$ , but all of the best determinations lead to a mean number higher than is admissible under the currently accepted hypotheses. Whether theory or experiment is at fault remains to be discovered.

The first, and for many years the only, determinations of the constant in question were made by Berzelius.\* By means of nitric acid he oxidized tellurium to the dioxide, and from the increase in weight deduced a value for the metal. He published only his final results, from which, if  $\text{O} = 100$ ,  $\text{Te} = 802.121$ . The three separate experiments give  $\text{Te} = 801.74$ ,  $801.786$ , and  $802.838$ , whence we can calculate the following percentages of metal in the dioxide:

80.057
80.036
80.034
Mean, 80.042, $\pm .005$

The next determinations were made by von Hauer,† who resorted to the analysis of the well crystallized double salt  $\text{TeBr}_4 \cdot 2\text{KBr}$ . In this compound the bromine was estimated as silver bromide, the values assumed for Ag and Br being respectively 108.1 and 80. Recalculating, with our newer atomic weights for the above-named elements, we get from von Hauer's analyses, for 100 parts of the salt, the quantities of AgBr which are put in the third column:

2.000	gram. $\text{K}_2\text{TeBr}_6$ gave	69.946	per cent. Br.	164.460
6.668	“	69.8443	“	164.221
2.934	“	69.9113	“	164.379
3.697	“	70.0163	“	164.626
1.000	“	69.901	“	164.355
				Mean, 164.408, $\pm .045$

From Berzelius' series we may calculate  $\text{Te} = 127.366$ , and from von Hauer's  $\text{Te} = 126.454$ . Dumas,‡ by a method for which he gives absolutely no particulars, found  $\text{Te} = 129$ .

In 1879, with direct reference to Mendelejeff's theory, the subject of the atomic weight of tellurium was taken up by Wills.§ The methods

\* Poggend. Annalen, 28, 395. 1833.

† Sitzungsab. Wien Akad., 25, 142.

‡ Ann. Chim. Phys. (3), 55, 129. 1859.

§ Journ. Chem. Soc., Oct., 1879, p. 704.

of Berzelius and von Hauer were employed, with various rigid precautions in the way of testing balance and weights, and to ensure purity of material. In the first series of experiments tellurium was oxidized by nitric acid to form  $\text{TeO}_2$ . The results gave figures ranging from  $\text{Te} = 125.64$  to  $128.66$ :

2.21613	gram.	Te gave	2.77612	gram.	$\text{TeO}_2$ .	79.828	per cent.	Te.
1.45313	"		1.81542	"		80.044	"	
2.67093	"		3.33838	"		80.007	"	
4.77828	"		5.95748	"		80.207	"	
2.65029	"		3.31331	"		79.989	"	

Mean,  $80.015, \pm .041$

In the second series tellurium was oxidized by aqua regia to  $\text{TeO}_2$ , with results varying from  $\text{Te} = 127.10$  to  $127.32$ :

2.85011	gram.	Te gave	3.56158	gram.	$\text{TeO}_2$ .	80.024	per cent.	Te.
3.09673	"		3.86897	"		80.040	"	
5.09365	"		6.36612	"		80.012	"	
3.26604	"		4.08064	"		80.037	"	

Mean,  $80.028, \pm .004$

By von Hauer's process, the analysis of  $\text{TeBr}_4 \cdot 2\text{KBr}$ , Will's figures give results ranging from  $\text{Te} = 125.40$  to  $126.94$ . Reduced to a common standard, 100 parts of the salt yield the quantities of  $\text{AgBr}$  given in the third column:

1.70673	gram.	$\text{K}_2\text{TeBr}_6$ gave	2.80499	gram.	$\text{AgBr}$ .	164.349
1.75225	"		2.88072	"		164.398
2.06938	"		3.40739	"		164.657
3.29794	"		5.43228	"		164.717
2.46545	"		4.05742	"		164.571

Mean,  $164.538, \pm .048$

Combined with von Hauer's mean,  $164.408, \pm .045$ , this gives a general mean of  $164.468, \pm .033$ . Hence  $\text{Te} = 126.502$ .

The next determinations in order of time were those of Brauner.\* This chemist tried various unsuccessful methods for determining the atomic weight of tellurium, among them being the synthetic preparation of silver, copper, and gold tellurides, and the basic sulphate,  $\text{Te}_2\text{SO}_7$ . None of these methods gave sufficiently concordant results, and they were therefore abandoned. The oxidation of tellurium to dioxide by means of nitric acid was also unsatisfactory, but a series of oxidations with aqua regia gave data as follows. The third column contains the percentage of tellurium in the dioxide:

\* Journ. Chem. Soc., 55, 382. 1889.

<i>Te.</i>	<i>TeO<sub>2</sub>.</i>	<i>Per cent. Te.</i>
2.3092	2.9001	79.625
2.8153	3.5332	79.681
4.0176	5.0347	79.798
3.1613	3.9685	79.660
.8399	1.0526	79.793

Mean, 79.711,  $\pm$  .0239

Hence  $\text{Te} = 124.709$ .

In a single analysis of the dioxide, by reduction with  $\text{SO}_2$ , 2.5489 grammes  $\text{TeO}_2$  gave 2.0374 of metal. If we give this experiment the weight of one observation in the synthetic series, the percentage of tellurium found by it becomes—

79.932,  $\pm$  .0534.

Hence  $\text{Te} = 126.494$ .

Brauner's best results were obtained from analyses of tellurium tetrabromide, prepared from pure tellurium and pure bromine, and afterwards sublimed in a vacuum. This compound was titrated with standard solutions of silver, and three series of experiments, made with samples of bromide of different origin, gave results as follows. The  $\text{TeBr}_4$  equivalent to 100 parts of silver appears in the third column:

*First Series.*

<i>TeBr<sub>4</sub>.</i>	<i>Ag<sub>4</sub>.</i>	<i>Ratio.</i>
2.14365	2.06844	103.636
1.76744	1.70531	103.643
1.47655	1.42477	103.634
1.23354	1.19019	103.642

*Second Series.*

<i>TeBr<sub>4</sub>.</i>	<i>Ag<sub>4</sub>.</i>	<i>Ratio.</i>
3.07912	2.97064	103.651
5.47446	5.28157	103.652
3.30927	3.19313	103.637
7.26981	7.01414	103.645
3.52077	3.39667	103.654

*Third Series.*

<i>TeBr<sub>4</sub>.</i>	<i>Ag<sub>4</sub>.</i>	<i>Ratio.</i>
2.35650	2.27363	103.645
1.51931	1.46564	103.662
1.43985	1.38942	103.630

Mean of all as one series, 103.644,  $\pm$  .0018

Hence  $\text{Te} = 126.668, \pm .0290$ . A reduction of the weighings to a vacuum raises this by 0.07 to 126.738.

Still another series of analyses, made with fractionated material, gave values for tellurium running up to as high as 137. These experiments led Brauner to believe that he had found in tellurium a higher homologue of that element, a view which he has since abandoned.\* Brauner also made a series of analyses of tellurium dibromide, but the results were unsatisfactory.

In the series of determinations by Gooch and Howland† an alkaline solution of tellurium dioxide was oxidized by means of standard solutions of potassium permanganate. This was added in excess, the excess being measured, after acidification with sulphuric acid, by back titration with oxalic acid and permanganate. Two series are given, varying in detail, but for present purposes they may be treated as one. The ratio  $\text{TeO}_2 : \text{O} : : 100 : x$  is given in the third column.

<i>TeO<sub>2</sub> Taken.</i>	<i>O Required.</i>	<i>Ratio.</i>
.1200	.01202	10.017
.0783	.00785	10.026
.0931	.00940	10.097
.1100	.01119	10.149
.0904	.00909	10.055
.1065	.01078	10.122
.0910	.00915	10.055
.0910	.00910	10.000
.0911	.00924	10.143
.0913	.00915	10.022
.0912	.00915	10.033
.0914	.00923	10.098

Mean, 10.068,  $\pm .0100$

Hence  $\text{Te} = 125.96$ .

In Staudenmaier's‡ determinations of the atomic weight of tellurium, crystallized telluric acid,  $\text{H}_6\text{TeO}_6$  was the starting point. By careful heating in a glass bulb this compound can be reduced to  $\text{TeO}_2$ , and by heating in hydrogen, to metal. In the latter case finely divided silver was added to prevent volatilization of tellurium. The telluric acid was fractionally crystallized, but the different fractions gave fairly constant results. I therefore group Staudenmaier's data so as to bring them into series more suitable for the present discussion.

\* Journ. Chem. Soc., 67, 549. 1895.

† Amer. Journ. Sci., 58, 375. 1894. Some misprints in the original publication have been kindly corrected by Professor Gooch; hence the differences between these data and the figures formerly given.

‡ Zeitsch. Anorg. Chem., 10, 189. 1895.

*First.  $H_6TeO_6$  to  $TeO_2$ .*

$H_6TeO_6$ .	Loss in Weight.	Per cent. $TeO_2$ .
1.7218	.5260	69.451
2.8402	.8676	69.453
4.0998	1.2528	69.442
3.0916	.9450	69.433
1.1138	.3405	69.429
4.9843	1.5236	69.432
4.6716	1.4278	69.437

---

Mean, 69.440,  $\pm$  .0024

Hence  $Te = 126.209$ .

*Second.  $H_6TeO_6$  to  $Te$ .*

$H_6TeO_6$ .	Loss in Weight.	Per cent. $Te$ .
1.2299	.5471	55.517
1.0175	.4526	55.518
2.5946	1.1549	55.488

---

Mean, 55.508,  $\pm$  .0068

Hence  $Te = 126.303$ .

Staudenmaier also gives four reductions of  $TeO_2$  to  $Te$ , in presence of finely divided silver. The data are as follows:

$TeO_2$ .	Loss in Weight.	Per cent. $Te$ .
.9171	.1839	79.948
1.9721	.3951	79.966
2.4115	.4835	79.950
1.0172	.2041	79.935

---

Mean, 79.950,  $\pm$  .0043

Hence  $Te = 126.636$ .

The last series, giving the percentage of tellurium in the dioxide, combines with previous series thus:

Berzelius.....	80.042, $\pm$ .0050
Wills, first series.....	80.015, $\pm$ .0410
Wills, second series.....	80.028, $\pm$ .0040
Brauner, synthesis.....	79.711, $\pm$ .0239
Brauner, analysis.....	79.932, $\pm$ .0534
Staudenmaier.....	79.950, $\pm$ .0043
General mean.....	80.001, $\pm$ .0025

The very recent determinations by Chikashigé\* were made by Brauner's method, giving the ratio between silver and  $TeBr_4$ . In all essential particulars the work resembles that of Brauner, except that the tellurium,

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\* Journ. Chem. Soc., 69, 881. 1896.

instead of being extracted from metallic tellurides, was derived from Japanese native sulphur, in which it exists as an impurity. This difference of origin in the material studied gives the chief interest to the investigation. The data are as follows:

<i>TeBr<sub>4</sub></i>	<i>Ag.</i>	<i>Ratio.</i>
4.1812	4.0348	103.628
4.3059	4.1547	103.639
4.5929	4.4319	103.633
		Mean, 103.633, $\pm .0023$
		Brauner found, 103.644, $\pm .0018$
		General mean, 103.640, $\pm .0014$

Now, to sum up, the subjoined ratios are available for computing the atomic weight of tellurium:

- (1.) Percentage Te in  $\text{TeO}_2$ , 80.001,  $\pm .0025$
- (2.) Percentage Te in  $\text{H}_6\text{TeO}_6$ , 55.508,  $\pm .0068$
- (3.) Percentage  $\text{TeO}_2$  in  $\text{H}_6\text{TeO}_6$ , 64.440,  $\pm .0024$
- (4.)  $\text{Ag}_4 : \text{TeBr}_4 :: 100 : 103.640$ ,  $\pm .0014$
- (5.)  $\text{K}_2\text{TeBr}_6 : 6\text{AgBr} :: 100 : 164.468$ ,  $\pm .0330$
- (6.)  $\text{TeO}_2 : \text{O} :: 100 : 10.068$ ,  $\pm .0100$

To reduce these ratios we have—

O = 15.879, $\pm .0003$	K = 38.817, $\pm .0051$
Ag = 107.108, $\pm .0031$	AgBr = 186.452, $\pm .0054$
Br = 79.344, $\pm .0062$	

For the atomic weight of tellurium six values appear, as follows:

From (1).....	Te = 127.040, $\pm .0165$
From (4).....	" = 126.650, $\pm .0302$
From (5).....	" = 126.502, $\pm .1430$
From (2). . . . .	" = 126.303, $\pm .0246$
From (3).....	" = 126.209, $\pm .0138$
From (6).....	" = 125.960, $\pm .1574$
General mean.....	Te = 126.523, $\pm .0092$

If O = 16, Te = 127.487.

A careful consideration of the foregoing figures, and of the experimental methods by which they were obtained, will show that they are not absolutely conclusive with regard to the place of tellurium under the periodic law. The atomic weight of iodine, calculated in a previous chapter, is 125.888. Wills' values for Te, rejecting his first series as relatively unimportant, range from 125.40 to 127.32; that is, some of them fall below the atomic weight of iodine, although none descend quite to the 125 assumed by Mendelejeff.

Some of Brauner's data fall even lower; and the same thing is true in



Gooch and Howland's series, of which the mean gives  $\text{Te} = 125.96$ , a value very little above that of iodine.

In considering the experimental methods, reference may properly be made to the controversy regarding the atomic weight of antimony. It will be seen that Dexter, estimating the latter constant by the conversion of the metal into  $\text{Sb}_2\text{O}_3$ , obtained a value approximately of  $\text{Sb} = 122$ . Dumas, working with  $\text{SbCl}_3$ , obtained nearly the same value. Schneider and Cooke, on the other hand, have established an atomic weight for antimony near 120, and Cooke in particular has traced out the constant errors which lurked unsuspected in the work of Dumas. Now in their physical aspects tellurium and antimony are quite similar. The oxidation of tellurium to dioxide resembles in many particulars that of antimony, and may lead to error in the same way. In each of the six tellurium ratios there is still uncertainty, and a positive measurement, free from objections, of the constant in question is yet to be made.

## FLUORINE.

The atomic weight of fluorine has been chiefly determined by one general method, namely, by the conversion of fluorides into sulphates. The work of Christensen, however, is on different lines. Excluding the early results of Davy,\* we have to consider first the experiments of Berzelius, Louyet, Dumas, De Luca, and Moissan with reference to the fluorides of calcium, sodium, potassium, barium, and lead.

The ratio between calcium fluoride and sulphate has been determined by the five investigators above named, and by one general process. The fluoride is treated with strong sulphuric acid, the resulting sulphate is ignited, and the product weighed. In order to insure complete transformation special precautions are necessary, such, for instance, as repeated treatment with sulphuric acid, and so on. For details like these the original papers must be consulted.

The first experiments in chronological order are those of Berzelius,† who operated upon an artificial calcium fluoride. He found, in three experiments, for one part of fluoride the following of sulphate:

1.749

1.750

1.751

---

Mean, 1.750,  $\pm .0004$

Louyet's researches‡ were much more elaborate than the foregoing. He began with a remarkably concordant series of results upon fluor spar,

\* Phil. Trans., 1814, 64.

† Poggend. Annalen, 8, 1. 1826.

‡ Ann. Chim. Phys. (3), 25, 300. 1849.

in which one gramme of the fluoride yielded from 1.734 to 1.737 of sulphate. At first he regarded these as accurate, but he soon found that particles of spar had been coated with sulphate, and had therefore escaped action. In the following series this source of error was guarded against.

Starting with fluor spar, Louyet found of sulphate as follows :

1.742	
1.744	
1.745	
1.744	
1.7435	
1.7435	
<hr/>	
Mean,	1.7437, $\pm .0003$

A second series, upon artificial fluoride, gave :

1.743
1.741
1.741
<hr/>
Mean, 1.7417, $\pm .0004$

Dumas\* published but one result for calcium fluoride. .495 grm. gave .864 grm. sulphate, the ratio being 1 : 1.7455.

De Luca† worked with a very pure fluor spar, and published the following results. The ratio between  $\text{CaSO}_4$  and one gramme of  $\text{CaF}_2$  is given in the third column :

.9395 grm. $\text{CaF}_2$ gave	1.630 grm. $\text{CaSO}_4$ .	1.7518
.836	" 1.459 "	1.7452
.502	" .8755 "	1.7440
.3985	" .6945 "	1.7428

If we include Dumas' single result with these, we get a mean of 1.7459,  $\pm .0011$ .

Moissan‡ unfortunately gives no details nor weighings, but merely states that four experiments with calcium fluoride gave values for F ranging from 19.02 to 19.08. To S he assigned the value 32.074, and probably Ca was taken as = 40. With these data his extreme values as given may be calculated back into uniformity with the ratio as stated above, becoming—

1.7444
1.7410
<hr/>
Mean, 1.7427

\* Ann. Chem. Pharm., 113, 28. 1860.

† Compt. Rend., 51, 299. 1860.

‡ Compt. Rend., 111, 570. 1890.

If we assign this equal weight with Berzelius' series, the data for this ratio combine thus :

Berzelius . . . . .	1.7500, $\pm$ .0004
Louyet, first series . . . . .	1.7437, $\pm$ .0003
Louyet, second series . . . . .	1.7417, $\pm$ .0004
De Luca with Dumas . . . . .	1.7459, $\pm$ .0011
Moissan . . . . .	1.7427, $\pm$ .0004
General mean . . . . .	<u>1.7444, <math>\pm</math> .00018</u>

For the ratio between the two sodium salts we have experiments by Dumas, Louyet, and Moissan. According to Louyet, one gramme of NaF gives of  $\text{Na}_2\text{SO}_4$ —

1.686
1.683
1.685
<u>Mean, 1.6847, <math>\pm</math> .0006</u>

The weighings published by Dumas are as follows :

.777 gm. NaF give	1.312 gm. $\text{Na}_2\text{SO}_4$ .	Ratio, 1.689
1.737        "	2.930        "	"        1.687
		<u>Mean, 1.688, <math>\pm</math> .0007</u>

Moissan says only that five experiments with sodium fluoride gave  $\text{F} = 19.04$  to  $19.08$ . This was calculated with  $\text{Na} = 23.05$  and  $\text{S} = 32.074$ . Hence, reckoning backward, the two values give for the standard ratio—

1.6889
1.6873
<u>Mean, 1.6881</u>

Giving this equal weight with Dumas' mean, we have—

Louyet . . . . .	1.6847, $\pm$ .0006
Dumas . . . . .	1.688, $\pm$ .0007
Moissan . . . . .	1.6881, $\pm$ .0007
General mean . . . . .	<u>1.6867, <math>\pm</math> .00038</u>

Dumas also gives experiments upon potassium fluoride. The quantity of sulphate formed from one gramme of fluoride is given in the last column :

1.483 gm. KF give	2.225 gm. $\text{K}_2\text{SO}_4$ .	1.5002
1.309        "	1.961        "	1.4981
		<u>Mean, 1.4991, <math>\pm</math> .0007</u>

The ratio between barium fluoride and barium sulphate was measured

by Louyet and Moissan. According to Louyet, one gramme of  $\text{BaF}_2$  gives of  $\text{BaSO}_4$ —

$$\begin{array}{r} 1.332 \\ 1.331 \\ 1.330 \\ \hline \text{Mean, } 1.331, \pm .0004 \end{array}$$

Moissan, in five experiments, found  $F = 19.05$  to  $19.09$ . Assuming that he put  $\text{Ba} = 137$ , and  $S = 32.074$  as before, these two extremes become—

$$\begin{array}{r} 1.3311 \\ 1.3305 \\ \hline \text{Mean, } 1.3308 \end{array}$$

Giving this equal weight with Louyet's mean, we get the subjoined combination:

Louyet.....	1.331, $\pm .0004$
Moissan.....	1.3308, $\pm .0004$
General mean.....	1.3309, $\pm .00028$

The experiments with lead fluoride are due to Louyet, and a new method of treatment was adopted. The salt was fused, powdered, dissolved in nitric acid, and precipitated by dilute sulphuric acid. The evaporation of the fluid and the ignition of the sulphate was then effected without transfer. Five grammes of fluoride were taken in each operation, yielding of sulphate:

$$\begin{array}{r} 6.179 \\ 6.178 \\ 6.178 \\ \hline \text{Mean, } 6.1783, \pm .0002 \end{array}$$

In Christensen's determinations\* we find a method adopted which is radically unlike anything in the work of his predecessors. He started out with the salt  $(\text{NH}_4)_2\text{MnF}_5$ . When this is added to a mixture, in solution, of potassium iodide and hydrochloric acid, iodine is set free, and may be titrated with sodium thiosulphate. One molecule of the salt (as written above), liberates one atom of iodine. In four experiments Christensen obtained the following data:

3.1199 grm. $\text{Am}_2\text{MnF}_5$ gave	2.12748 I.	68.191 per cent.
3.9190                   “	2.67020 “	68.135   “
3.5005                   “	2.38429 “	68.113   “
1.2727                   “	.86779 “	68.185   “
		Mean, 68.156, $\pm .0128$

\* Journ. für Prakt. Chem. (2), 35, 541. Christensen assigns to the salt double the formula here given.

The ratios from which to compute the atomic weight of fluorine are now—

- (1.)  $\text{CaF}_2 : \text{CaSO}_4 :: 1.0 : 1.7444, \pm .00018$
- (2.)  $2\text{NaF} : \text{Na}_2\text{SO}_4 :: 1.0 : 1.6867, \pm .00038$
- (3.)  $2\text{KF} : \text{K}_2\text{SO}_4 :: 1.0 : 1.4991, \pm .0007$
- (4.)  $\text{BaF}_2 : \text{BaSO}_4 :: 1.0 : 1.3309, \pm .00028$
- (5.)  $\text{PbF}_2 : \text{PbSO}_4 :: 5.0 : 6.1783, \pm .0002$
- (6.)  $\text{Am}_2\text{MnF}_5 : \text{I} :: 100 : 68.156, \pm .0128$

To reduce them we have—

O = 15.879, $\pm .0003$	K = 38.817, $\pm .0051$
S = 31.828, $\pm .0015$	Ca = 39.764, $\pm .0045$
N = 13.935, $\pm .0021$	Ba = 136.392, $\pm .0086$
I = 125.888, $\pm .0069$	Pb = 205.358, $\pm .0040$
Na = 22.881, $\pm .0046$	Mn = 54.571, $\pm .0013$

And the values derived for fluorine are as follows :

From (1).....	F = 18.844, $\pm .0048$
From (2).....	" = 18.948, $\pm .0108$
From (3).....	" = 18.877, $\pm .0276$
From (4).....	" = 18.869, $\pm .0192$
From (5).....	" = 18.997, $\pm .0047$
From (6).....	" = 18.853, $\pm .0073$
—	
General mean.....	F = 18.912, $\pm .0029$

If O = 16, F = 19.056.

In all probability these values for fluorine average a trifle too high. It is difficult to be certain that a fluoride has been completely converted into sulphate, and an incomplete conversion tends to raise the apparent atomic weight of fluorine. This possible source of error exists in all of the ratios except the last one, but the fair concordance of the results obtained seems to indicate that the uncertainty cannot be very large.

## MANGANESE.

The earliest experiments of Berzelius\* and of Arfvedson† gave values for Mn ranging between 56 and 57, and therefore need no farther consideration here. The first determinations to be noticed are those of Turner‡ and a later measurement by Berzelius,§ who both determined gravimetrically the ratio between the chlorides of manganese and silver. The manganese chloride was fused in a current of dry hydrochloric acid, and afterwards precipitated with a silver solution. I give the  $\text{MnCl}_2$  equivalent to 100 parts of  $\text{AgCl}$  in the third column:

4.20775 grm. $\text{MnCl}_2$	=	9.575 grm. $\text{AgCl}$ .	43.945	} Berzelius.
3.063        "        "	=	6.96912        "        "	43.950	
12.47 grains $\text{MnCl}_2$	=	28.42 grains $\text{AgCl}$ .	43.878	—Turner.
Mean, 43.924, $\pm .015$				

Many years later Dumas|| also made the chloride of manganese the starting point of some atomic weight determinations. The salt was fused in a current of hydrochloric acid, and afterwards titrated with a standard solution of silver in the usual way. One hundred parts of Ag are equivalent to the quantities of  $\text{MnCl}_2$  given in the third column:

3.3672 grm. $\text{MnCl}_2$	=	5.774 grm. Ag.	58.317
3.0872        "        "	=	5.293        "        "	58.326
2.9671        "        "	=	5.0875        "        "	58.321
1.1244        "        "	=	1.928        "        "	58.320
1.3134        "        "	=	2.251        "        "	58.321
Mean, 58.321, $\pm .001$			

An entirely different method of investigation was followed by von Hauer,¶ who, as in the case of cadmium, ignited the sulphate in a stream of sulphuretted hydrogen, and determined the quantity of sulphide thus formed. I subjoin his weighings, and also the percentage of MnS in  $\text{MnSO}_4$  as calculated from them:

4.0626 grm. $\text{MnSO}_4$	gave	2.3425 grm. MnS.	57.660 per cent.
4.9367        "        "		2.8442        "        "	57.613        "        "
5.2372        "        "		3.0192        "        "	57.649        "        "
7.0047        "        "		4.0347        "        "	57.600        "        "
4.9175        "        "		2.8297        "        "	57.543        "        "
4.8546        "        "		2.7955        "        "	57.585        "        "
4.9978        "        "		2.8799        "        "	57.625        "        "
4.6737        "        "		2.6934        "        "	57.629        "        "
4.7240        "        "		2.7197        "        "	57.572        "        "
Mean, 57.608, $\pm .008$			

\* Poggend. Annalen, 8, 185. 1826.

† Berz. Jahresbericht, 9, 136. 1829.

‡ Trans. Roy. Soc. Edinb., 11, 143. 1831.

§ Lehrbuch, 5 Aufl., 3, 1224.

|| Ann. Chem. Pharm., 113, 25. 1860.

¶ Journ. für Prakt. Chem., 72, 360. 1857.

This method of von Hauer, which seemed to give good results with cadmium, is, according to Schneider,\* inapplicable to manganese, for the reason that the sulphide of the latter metal is liable to be contaminated with traces of oxysulphide. Such an impurity would bring the atomic weight out too high. The results of two different processes, one carried out by himself and the other in his laboratory by Rawack, are given by Schneider in this paper.

Rawack reduced manganoso-manganic oxide to manganous oxide by ignition in a stream of hydrogen, and weighed the water thus formed. From his weighings I get the values in the third column, which represent the  $Mn_3O_4$  equivalent to one gramme of water:

4.149	gram.	$Mn_3O_4$	gave	0.330	gram.	$H_2O$ .	12.5727
4.649	"			.370	"		12.5643
6.8865	"			.5485	"		12.5552
7.356	"			.5855	"		12.5636
8.9445	"			.7135	"		12.5361
11.584	"			.9225	"		12.5572
							Mean, 12.5582, $\pm .0034$

Here the most obvious source of error lies in the possible loss of water. Such a loss, however, would increase the apparent atomic weight of manganese; but we see that the value found is much lower than that obtained either by Dumas or von Hauer.

Schneider himself effected the combustion of manganous oxalate with oxide of copper. The salt was not absolutely dry, so that it was necessary to collect both water and carbon dioxide. Then, upon deducting the weight of water from that of the original material, the weight of anhydrous oxalate was easily ascertained. Subtracting from this the  $CO_2$ , we get the weight of Mn. If we put  $CO_2 = 100$ , the quantities of manganese equivalent to it will be found in the last column:

1.5075	gram.	oxalate	gave	.306	gram.	$H_2O$ and	.7445	gram.	$CO_2$ .	61.3835
2.253	"			.4555	"		1.1135	"		61.4291
3.1935	"			.652	"		1.5745	"		61.4163
5.073	"			1.028	"		2.507	"		61.3482
										Mean, 61.3943, $\pm .0122$

Up to this point the data give two distinct values for Mn—one near 54, the other approximately 55—and with no sure guide to preference between them. The higher value, however, has been confirmed by later testimony.

In 1883 Dewar and Scott† published the results of their work upon silver permanganate. This salt is easily obtained pure by recrystallization, and has the decided advantage of not being hygroscopic. Two sets

\* Poggend. Annalen, 107, 605.

† Proc. Roy. Soc., 35, 44. 1883.

of experiments were made. First, the silver permanganate was heated to redness in a glass bulb, first in air, then in hydrogen. Before weighing, the latter gas was replaced by nitrogen. The data are as follows:

$AgMnO_4$ .	$Ag + MnO$ .	Per cent. $Ag + MnO$ .
5.8696	4.63212	78.917
5.4988	4.33591	78.852
7.6735	6.05395	78.894
13.10147	10.31815	78.756
12.5799	{ 9.91065	78.782
	{ 9.91435	78.811
		Mean, 78.835, $\pm .0174$

The duplication of the last weighing is not explained.

In the second series the permanganate was dissolved in dilute nitric acid, reduced by sulphur dioxide, potassium nitrite, or sodium formate, and titrated with potassium bromide. The  $AgMnO_4$  equivalent to 100 KBr appears in the third column.

$AgMnO_4$ .	KBr.	Ratio.
6.5289	3.42385	190.686
7.5378	3.9553	190.575
6.1008	3.20166	190.559
5.74647	3.00677	191.117
6.16593	3.23602	190.540
5.11329	2.6828	190.596
5.07438	2.66204	190.624
13.4484	7.05602	190.604
12.5799	6.60065	190.588
12.27025	6.43808	190.584
		Mean, 190.647, $\pm .0361$

Vacuum weights are given throughout. To the first series of experiments the authors attach little importance, and numbers 1 and 4 of the second series they also regard as questionable. These experiments represent the use of sulphur dioxide as the reducing agent, and were attended by the formation of an insoluble residue, apparently of a sulphide. Excluding them, the remaining eight experiments of the second series give in mean—

$$KBr : AgMnO_4 :: 100 : 190.584, \pm .0062,$$

which will be used for the present calculation. Dewar and Scott also made determinations with manganese chloride and bromide. With the first salt they found  $Mn = 54.91$ , and with the second,  $Mn = 54.97$ ; but they give no details.

Marignac's work upon the atomic weight of manganese also appeared in 1883.\* He prepared the oxide,  $MnO$ , by ignition of the oxalate and

\*Arch. Sci. Phys. et Nat. (3), 10, 21. 1883.



subsequent reduction of the resulting  $\text{Mn}_3\text{O}_4$  in hydrogen. The oxide, with various precautions, was then converted into sulphate. The percentage of  $\text{MnO}$  in  $\text{MnSO}_4$  is appended:

2.6587	grm.	$\text{MnO}$	gave	5.6530	$\text{MnSO}_4$ .	47.032	per cent.
2.5185		"		5.3600	"	46.987	"
2.5992		"		5.5295	"	47.006	"
2.8883		"		6.1450	"	47.002	"

Mean, 47.007,  $\pm .0025$

J. M. Weeren, in 1890,\* published determinations made by two methods, the one Marignac's, the other von Hauer's. From manganese sulphate he threw down the hydrated peroxide electrolytically, and the latter compound was then reduced in hydrogen which had been proved to be free from oxygen. The resulting monoxide was cooled in a stream of purified nitrogen. After the oxide had been treated with sulphuric acid, converted into sulphate, and weighed, a few drops of sulphuric acid and a little sulphurous acid were added to it, after which it was reheated and weighed again. This process was repeated until four successive weighings absolutely agreed. The results of this set of experiments were as follows, with vacuum standards:

15.2349	grm.	$\text{MnO}$	gave	32.4142	$\text{MnSO}_4$ .	47.005	per cent.
13.9686		"		29.7186	"	47.004	"
13.7471		"		29.2493	"	47.000	"
15.5222		"		33.0246	"	47.001	"
14.9824		"		31.8755	"	47.002	"
14.6784		"		31.2304	"	47.000	"

Mean, 47.002,  $\pm .0006$

Marignac's mean, combined with this, hardly affects either the percentage itself or its probable error. Fortunately, both Marignac and Weeren are completely in agreement as to the ratio, and either set of measurements would be valid without the other. In order, therefore, to give Marignac's work some proper recognition, we can assume a general mean of 47.004,  $\pm .0006$ , without danger of serious error.

The manganese sulphate produced in the foregoing series of experiments was used, with many precautions, for the next series carried out by von Hauer's method. It was transferred to a porcelain boat, dried at  $260^\circ$  to avoid errors due to retention of water taken up in the process of transfer, and then heated to constant weight in a stream of hydrogen sulphide. Before weighing, the sulphide was heated to redness in hydrogen and cooled in the same gas. The results, with vacuum weights, were as follows:

\* Atom-Gewichtsbestimmung des Mangans. Inaugural Dissertation, Halle, 1890.

16.0029	grm. $\text{MnSO}_4$	gave 9.2228	$\text{MnS} = 57.632$	per cent.
16.3191	"	9.4048	"	57.631 "
15.9307	"	9.1817	"	57.634 "
15.8441	"	9.1315	"	57.634 "
16.2783	"	9.3819	"	57.635 "
17.0874	"	9.8477	"	57.633 "

Mean,  $57.633, \pm .0004$   
 von Hauer found,  $57.608, \pm .0080$

Hence the general mean is identical with Weeren's to the third decimal place, which is unaffected by combination with von Hauer's data.

We have now to consider the following ratios for manganese:

- (1.)  $2\text{AgCl} : \text{MnCl}_2 :: 100 : 41.924, \pm .0150$
- (2.)  $2\text{Ag} : \text{MnCl}_2 :: 100 : 58.321, \pm .0010$
- (3.)  $\text{H}_2\text{O} : \text{Mn}_3\text{O}_4 :: 100 : 1255.82, \pm .340$
- (4.)  $2\text{CO}_2 : \text{Mn} :: 100 : 61.3943, \pm .0122$
- (5.)  $\text{AgMnO}_4 : \text{Ag} + \text{MnO} :: 100 : 78.835, \pm .0174$
- (6.)  $\text{KBr} : \text{AgMnO}_4 :: 100 : 190.584, \pm .0062$
- (7.)  $\text{MnSO}_4 : \text{MnO} :: 100 : 47.004, \pm .0006$
- (8.)  $\text{MnSO}_4 : \text{MnS} :: 100 : 57.633, \pm .0004$

Computing with the subjoined preliminary data—

O = 15.879, $\pm .0003$	K = 38.817, $\pm .0051$
Ag = 107.108, $\pm .0031$	C = 11.920, $\pm .0004$
Cl = 35.179, $\pm .0048$	S = 31.828, $\pm .0015$
Br = 79.344, $\pm .0062$	AgCl = 142.287, $\pm .0037$

these ratios reduce as follows:

First, for the molecular weight of manganese chloride, two values are deducible.

From (1) .....	$\text{MnCl}_2 = 124.996, \pm .0428$
From (2) .....	" = $124.933, \pm .0042$
General mean .....	$\text{MnCl}_2 = 124.934, \pm .0042$

Hence  $\text{Mn} = 54.576, \pm .0075$ .

For manganese there are seven independent values, as follows:

From molecular weight $\text{MnCl}_2$ .....	$\text{Mn} = 54.576, \pm .0075$
From (3) .....	" = $53.667, \pm .0203$
From (4) .....	" = $53.633, \pm .0107$
From (5) .....	" = $54.450, \pm .1511$
From (6) .....	" = $54.572, \pm .0173$
From (7) .....	" = $54.601, \pm .0018$
From (8) .....	" = $54.575, \pm .0022$
General mean .....	$\text{Mn} = 54.571, \pm .0013$

If  $\text{O} = 16$ , this becomes  $\text{Mn} = 54.987$ .

In this case five of the separate values are well in accord, and the rejection of the two aberrant values, which have high probable errors, is

not necessary. Their influence is imperceptible. Weeren's marvelously concordant data seem to receive undue weight, but they are abundantly confirmed by the evidence of other experimenters. In short, the atomic weight of manganese appears to be quite well determined.

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## IRON.

The atomic weight of iron has been mainly determined from the composition of ferric oxide, with some rather scanty data relative to other compounds.

Most of the earlier data relative to the percentage of metal and oxygen in ferric oxide we may reject at once, as set aside by later investigations. Among this no longer valuable material there is a series of experiments by Berzelius, another by Döbereiner, and a third by Capitaine. The work done by Stromeyer and by Wackenroder was probably good, but I am unable to find its details. The former found 30.15 per cent. of oxygen in the oxide under consideration, while Wackenroder obtained figures ranging from a minimum of 30.01 to a maximum of 30.38 per cent.\*

In 1844 Berzelius † published two determinations of the ratio in question. He oxidized iron by means of nitric acid, and weighed the oxide thus formed. He thus found that when  $O = 100$   $Fe = 350.27$  and  $350.369$ .

Hence the following percentages of Fe in  $Fe_2O_3$ :

$$\begin{array}{r} 70.018 \\ 70.022 \\ \hline \text{Mean, } 70.020, \pm .0013 \end{array}$$

About the same time Svanberg and Norlin ‡ published two elaborate series of experiments; one relating to the synthesis of ferric oxide, the other to its reduction. In the first set pure piano-forte wire was oxidized by nitric acid, and the amount of oxide thus formed was determined. The results were as follows:

1.5257	gram. Fe gave 2.1803	gram. $Fe_2O_3$ .	69.977	per cent. Fe.
2.4051	"	3.4390	"	69.936
2.3212	"	3.3194	"	69.928
2.32175	"	3.3183	"	69.968
2.2772	"	3.2550	"	69.960
2.4782	"	3.5418	"	69.970
2.3582	"	3.3720	"	69.935
				<hr/>
				Mean, 69.9534, $\pm .0050$

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\* For additional details concerning these earlier papers I must refer to Oudemans' monograph, pp. 149, 141.

† Ann. Chem. Pharm., 30, 432. Berz. Jahresb., 25, 43.

‡ Berzelius' Jahresbericht, 25, 42.

In the second series ferric oxide was reduced by ignition in a current of hydrogen, yielding the subjoined percentages of metal :

2.98353	gram.	$\text{Fe}_2\text{O}_3$	gave	2.08915	gram.	Fe.	70.025	per cent.
2.41515		"		1.6910		"	70.015	"
2.99175		"		2.09455		"	70.014	"
3.5783		"		2.505925		"	70.030	"
4.1922		"		2.9375		"	70.072	"
3.1015		"		2.17275		"	70.056	"
2.6886		"		1.88305		"	70.036	"

Mean, 70.0354,  $\pm .0055$

It is evident that one or both of these series must be vitiated by constant errors, and that these probably arise from impurities in the materials employed. Impurities in the wire taken for the oxidation series could hardly have been altogether avoided, and in the reduction series it is possible that weighable traces of hydrogen may have been retained by the iron. At all events, it is probable that the errors of both series are in contrary directions, and therefore in some measure compensatory.

In 1844 there was also published an important paper by Erdmann and Marchand.\* These chemists prepared ferric oxide by the ignition of pure ferrous oxalate, and submitted it to reduction in a stream of hydrogen. Two sets of results were obtained with two different samples of ferrous oxalate, prepared by two different methods. For present purposes, however, it is not necessary to discuss these sets separately. The percentages of iron in  $\text{Fe}_2\text{O}_3$  are as follows :

70.013	} A.
69.962	
69.979	
70.030	
69.977	
70.044	} B.
70.015	
70.055	

Mean, 70.0094,  $\pm .0080$

In 1850 Maumené's† results appeared. He dissolved pure iron wire in aqua regia, precipitated with ammonia, filtered off the precipitate, washed thoroughly, ignited, and weighed, after the usual methods of quantitative analysis. The percentages of Fe in  $\text{Fe}_2\text{O}_3$  are given in the third column :

1.482	gram.	Fe	gave	2.117	gram.	$\text{Fe}_2\text{O}_3$ .	70.005	per cent.
1.452		"		2.074		"	70.010	"
1.3585		"		1.941		"	69.990	"
1.420		"		2.0285		"	70.002	"
1.492		"		2.1315		"	69.998	"
1.554		"		2.220		"	70.000	"

Mean, 70.0008,  $\pm .0019$

\* Journ. für Prakt. Chem., 33, 1. 1844.

† Compt. Rend., Oct. 17, 1850.

Two more results, obtained by Rivot\* through the reduction of ferric oxide in hydrogen, remain to be noticed. The percentages are:

$$\begin{array}{r} 69.31 \\ 69.35 \\ \hline \text{Mean, } 69.33, \pm .013 \end{array}$$

We have thus before us six series of results, which we may now combine:

Berzelius.....	70.020, $\pm .0013$
Erdmann and Marchand.....	70.0094, $\pm .0080$
Svanberg and Norlin, oxidation.....	69.9534, $\pm .0050$
Svanberg and Norlin, reduction.....	70.0354, $\pm .0055$
Maumené.....	70.0008, $\pm .0019$
Rivot.....	69.33, $\pm .013$
General mean.....	70.0075, $\pm .0010$

From this we get  $\text{Fe} = 55.596$ .

Dumas'† results, obtained from the chlorides of iron, are of so little weight that they might safely be omitted from our present discussion. For the sake of completeness, however, they must be included.

Pure ferrous chloride, ignited in a stream of hydrochloric acid gas, was dissolved in water and titrated with a silver solution in the usual way. One hundred parts of silver are equivalent to the amounts of  $\text{FeCl}_2$  given in the third column:

3.677 grm. $\text{FeCl}_2 = 6.238$ grm. Ag.	58.945
3.924     "     = 6.675     "	58.787
	<hr/>
Mean, 58.866, $\pm .053$	

Ferric chloride, titrated in the same way, gave these results:

1.179 grm. $\text{FeCl}_3 = 2.3475$ grm. Ag.	50.224
1.242     "     = 2.471     "	50.263
	<hr/>
Mean, 50.2435, $\pm .0132$	

These give us two additional values for Fe, as follows:

From $\text{FeCl}_2$ .....	$\text{Fe} = 55.742$
From $\text{FeCl}_3$ .....	" = 55.907

A series of determinations of the equivalent of iron, made by students by measuring the hydrogen evolved when the metal is dissolved in an acid, was published by Torrey in 1888.‡ The data have, of course, slight

\* Ann. Chem. Pharm., 78, 214. 1851.

† Ann. Chem. Pharm., 113, 26. 1860.

‡ Am. Chem. Journ., 10, 74.

value, but may be considered as being in some measure confirmatory. They are as follows :

56.40
55.60
55.38
55.56
55.48
55.50
55.86
56.06
56.22
55.80
55.78
55.60
55.70
55.94

Mean,  $55.777, \pm .0532$

These values undoubtedly depend on Regnault's value for the weight of hydrogen. Correcting by the later value, as found in the chapter of this work relating to the density ratio H : O, the mean becomes  $\text{Fe} = 55.608, \pm .0532$ . Here the probable error in the weight of the hydrogen is ignored, as being of no practical significance.

The four ratios for iron are now as follows :

- (1.) Per cent. Fe in  $\text{Fe}_2\text{O}_3$ ,  $70.0075, \pm .0010$
- (2.)  $\text{Ag}_2 : \text{FeCl}_2 :: 100 : 58.866, \pm .0530$
- (3.)  $\text{Ag}_3 : \text{FeCl}_3 :: 100 : 50.2435, \pm .0132$
- (4.) H : Fe : : 1 :  $55.608, \pm .0532$

Reducing these with—

$$\begin{aligned}\text{O} &= 15.879, \pm .0003 \\ \text{Ag} &= 107.108, \pm .0031 \\ \text{Cl} &= 35.179, \pm .0048\end{aligned}$$

we have—

From (1).....	Fe = $55.596, \pm .0023$
From (2).....	“ = $55.742, \pm .1140$
From (3).....	“ = $55.907, \pm .0450$
From (4).....	“ = $55.608, \pm .0532$
General mean.....	Fe = $55.597, \pm .0023$

If O = 16, then  $\text{Fe} = 56.021$ . Here all the values are absorbed practically by the first, the other three having no real significance.

## NICKEL AND COBALT.

On account of the close similarity of these metals to each other, their atomic weights, approximately if not actually identical, have received of late years much attention.

The first determinations, and the only ones up to 1852, were made by Rothhoff,\* each with but a single experiment. For nickel 188 parts of the monoxide were dissolved in hydrochloric acid; the solution was evaporated to dryness, the residue was dissolved in water, and precipitated by silver nitrate. 718.2 parts of silver chloride were thus formed; whence  $\text{Ni} = 58.613$ . The same process was applied also to cobalt, 269.2 parts of the oxide being found equivalent to 1029.9 of  $\text{AgCl}$ ; hence  $\text{Co} = 58.504$ . These values are so nearly equal that their differences were naturally ascribable to experimental errors. They are, however, entitled to no special weight at present, since it cannot be certain from any evidence recorded that the oxide of either metal was absolutely free from traces of the other.

In 1852 Erdmann and Marchand † published some results, but without details, concerning the atomic weight of nickel. They reduced the oxide by heating in a current of hydrogen, and obtained values ranging from 58.2 to 58.6, when  $\text{O} = 16$ . Their results were not very concordant, and the lowest was probably the best.

In 1856, incidentally to other work, Deville ‡ found that 100 parts of pure metallic nickel yielded 262 of sulphate; whence  $\text{Ni} = 58.854$ .

To none of the foregoing estimations can any importance now be attached. The modern discussion of the atomic weights under consideration began with the researches of Schneider § in 1857. This chemist examined the oxalates of both metals, determining carbon by the combustion of the salts with copper oxide in a stream of dry air. The carbon dioxide thus formed was collected as usual in a potash bulb, which, in weighing, was counterpoised by a similar bulb, so as to eliminate errors due to the hygroscopic character of the glass. The metal in each oxalate was estimated, first by ignition in a stream of dry air, followed by intense heating in hydrogen. Pure nickel or cobalt was left behind in good condition for weighing. Four analyses of each oxalate were made, with the results given below. The nickel salt contained three molecules of water, and the cobalt salt two molecules :

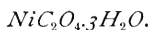
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\* Cited by Berzelius. Poggend. Annalen, 8, 184. 1826.

† Journ. für Prakt. Chem., 55, 202. 1852.

‡ Ann. Chim. Phys. (3), 46, 182. 1856.

§ Poggend. Annalen, 101, 387. 1857.



1.1945	gram.	gave	.528	gram.	CO <sub>2</sub> .	44.203	per cent.
2.5555	"		1.12625	"		44.072	"
3.199	"		1.408	"		44.014	"
5.020	"		2.214	"		44.104	"

Mean, 44.098,  $\pm$  .027

The following percentages of nickel were found in this salt :

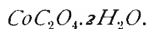
29.107

29.082

29.066

29.082

Mean, 29.084,  $\pm$  .006



1.6355	gram.	gave	.781	gram.	CO <sub>2</sub> .	47.753	per cent.
1.107	"		.5295	"		47.832	"
2.309	"		1.101	"		47.683	"
3.007	"		1.435	"		47.722	"

Mean, 47.7475,  $\pm$  .0213

The following were the percentages found for cobalt :

32.552

32.619

32.528

32.523

Mean, 32.5555,  $\pm$  .0149

In a later paper\* Schneider also gives some results obtained with a nickel oxalate containing but two molecules of water. This gave him 47.605 per cent. of CO<sub>2</sub>, and the following percentages of nickel :

31.4115

31.4038

Mean, 31.4076,  $\pm$  .0026

The conclusion at which Schneider arrived was that the atomic weights of cobalt and nickel are not identical, being about 60 and 58 respectively. The percentages given above will be discussed at the end of this chapter in connection with all the other data relative to the constants in question.

The next chemist to take up the discussion of these atomic weights was Marignac, in 1858.† He worked with the chlorides and sulphates

\* Poggend. Annalen, 107, 616.

† Arch. des Sci. Phys et Nat. (nouv. serie), 1, 372. 1858.



of nickel and cobalt, using various methods, but publishing few details, as he did not consider the determinations final. The sulphates, taken as anhydrous, were calcined to oxides. From the ratio  $\text{NiSO}_4 : \text{NiO}$ , he found  $\text{Ni} = 58.4$  to  $59.0$ , and from five measurements of the ratio  $\text{CoSO}_4 : \text{Co}$ ,  $\text{Co} = 58.64$  to  $58.76$ . If oxygen is taken as 16, these give for the percentages of oxide in sulphate :

<i>CoO in CoSO<sub>4</sub>.</i>	<i>NiO in NiSO<sub>4</sub>.</i>
48.267	48.187
48.307	48.387
<hr/>	<hr/>
Mean, 48.287, $\pm .0135$	Mean, 48.287, $\pm .0675$

The chlorides were dried at  $100^\circ$ , but found to retain water; and in most cases were then either fused in a stream of chlorine or of dry, gaseous hydrochloric acid, or else calcined gently with ammonium chloride. The determinations were then made by titration with a standard solution of silver in nitric acid. Three experiments with anhydrous  $\text{CoCl}_2$  gave  $\text{Co} = 58.72$  to  $58.84$ . Three more with  $\text{CoCl}_2$  dried at  $100^\circ$  gave  $\text{Co} = 58.84$  to  $59.02$ . Three with anhydrous  $\text{NiCl}_2$  gave  $\text{Ni} = 58.80$  to  $59.00$ . If the calculations were made with  $\text{Ag} = 108$  and  $\text{Cl} = 35.5$ , then these data give as proportional to 100 parts of silver :

<i>NiCl<sub>2</sub>.</i>	<i>CoCl<sub>2</sub>.</i>
60.093	60.056
60.185	60.111
<hr/>	60.111
Mean, 60.139, $\pm .0310$	60.194
	<hr/>
	Mean, 60.118, $\pm .0192$

In one more experiment  $\text{NiCl}_2$  was precipitated with a known quantity of silver. The filtrate was calcined, yielding  $\text{NiO}$ ; hence the ratio  $\text{Ag}_2 : \text{NiO}$ , giving  $\text{Ni} = 59.29$ . This experiment needs no farther attention.

In short, according to Marignac, and contrary to Schneider's views, the two atomic weights are approximately the same. Marignac criticises Schneider's earlier paper, holding that the nickel oxalate may have contained some free oxalic acid, and that the cobalt salt was possibly contaminated with carbonate or with basic compounds. In his later papers Schneider rejects these suggestions as unfounded, and in turn criticises Marignac. The purity of anhydrous  $\text{NiSO}_4$  is not easy to guarantee, and, according to Schneider, the anhydrous chlorides of cobalt and nickel are liable to be contaminated with oxides. This is the case even when the chlorides are heated in chlorine, unless the gas is carefully freed from all traces of air and moisture.

Dumas'\* determinations of the two atomic weights were made with the chlorides of nickel and cobalt. The pure metals were dissolved in aqua regia, the solutions were repeatedly evaporated to dryness, and the residual chlorides were ignited in dry hydrochloric acid gas. The last two estimations in the nickel series were made upon  $\text{NiCl}_2$  formed by heating the spongy metal in pure chlorine. In the third column I give the  $\text{NiCl}_2$  or  $\text{CoCl}_2$  equivalent to 100 parts of silver:

.9123	gram.	$\text{NiCl}_2 = 1.515$	gram.	Ag.	60.218
2.295	"	3.8115	"	"	60.212
3.290	"	5.464	"	"	60.212
1.830	"	3.041	"	"	60.178
3.001	"	4.987	"	"	60.176
					<hr/>
					Mean, 60.1992, $\pm .0062$
2.352	gram.	$\text{CoCl}_2 = 3.9035$	gram.	Ag.	60.254
4.210	"	6.990	"	"	60.229
3.592	"	5.960	"	"	60.268
2.492	"	4.1405	"	"	60.186
4.2295	"	7.0255	"	"	60.202
					<hr/>
					Mean, 60.2278, $\pm .011$

These results give values for Co and Ni differing by less than a tenth of a unit; here, as elsewhere, the figure for Ni being a trifle the lower.

Combining these data with Marignac's, we have—

$$\text{Ag}_2 : \text{NiCl}_2 :: 100 : x.$$

Marignac.....	60.139, $\pm .0310$
Dumas.....	60.199, $\pm .0062$
<hr/>	
General mean .....	60.194, $\pm .0061$

$$\text{Ag}_2 : \text{CoCl}_2 :: 100 : x.$$

Marignac.....	60.118, $\pm .0192$
Dumas.....	60.228, $\pm .0110$
<hr/>	
General mean.....	60.200, $\pm .0095$

In 1863† the idea that nickel and cobalt have equal atomic weights was strengthened by the researches of Russell. He found that the black oxide of cobalt, by intense heating in an atmosphere of carbon dioxide, became converted into a brown monoxide of constant composition. The ordinary oxide of nickel, on the other hand, was shown to be convertible into a definite monoxide by simple heating over the blast lamp. The pure oxides of the two metals, thus obtained, were reduced by ignition in hydrogen, and their exact composition thus ascertained.

\* Ann. Chem. Pharm., 113, 25. 1860.

† Journ. Chem. Soc. (2), 1, 51. 1863.

Several samples of each oxide were taken, yielding the following data. The separate samples are indicated by lettering :

*Nickel.*

	<i>NiO.</i>	<i>Ni.</i>	<i>Per cent. Ni.</i>
A.	2.0820	1.6364	78.597
	2.0956	1.6468	78.584
	2.0148	1.5838	78.608
B.	2.2069	1.7342	78.581
	2.2843	1.7952	78.589
	2.1329	1.6761	78.583
C.	2.2783	1.7911	78.616
	2.1434	1.6845	78.590
	2.4215	1.9030	78.588
D.	2.1859	1.7179	78.590
	2.0088	1.5788	78.594
	2.0839	1.6379	78.597
	2.6560	2.0873	78.588

Mean, 78.593,  $\pm .0018$

*Cobalt.*

	<i>CoO.</i>	<i>Co.</i>	<i>Per cent. Co.</i>
A.	2.1211	1.6670	78.591
	2.0241	1.5907	78.588
	2.1226	1.6673	78.550
	1.9947	1.5678	78.598
	3.0628	2.4078	78.614
B.	2.1167	1.6638	78.603
	1.7717	1.3924	78.591
	1.7852	1.4030	78.591
C.	1.6878	1.3264	78.588
	2.2076	1.7350	78.592
D.	2.6851	2.1104	78.597
	2.1461	1.6868	78.598
E.	3.4038	2.6752	78.595
	2.2778	1.7901	78.589
	2.1837	1.7163	78.596

Mean, 78.592,  $\pm .0023$

These percentages are practically identical, and lead to essentially the same mean value for each atomic weight.

In a later paper Russell\* confirmed the foregoing results by a different process. He dissolved metallic nickel and cobalt in hydrochloric acid and measured the hydrogen evolved. Thus the ratio between the metal and the ultimate standard was fixed without the intervention of any other element. About two-tenths of a gramme of metal, or less, was

\* Journ. Chem. Soc. (2), 7, 494. 1867.

taken in each experiment. The data obtained were as follows; the last column giving the weight of hydrogen, computed from its volume, yielded by 100 parts of cobalt or nickel:

*Nickel.*

	<i>Wt. Ni.</i>	<i>Vol. H in cc.</i>	<i>Ratio.</i>
A.	{ .0906	153.62	3.420
	{ .1017	172.32	3.418
	{ .1990	337.06	3.416
	{ .0997	168.93	3.417
	{ .1891	319.86	3.412
	{ .1859	314.75	3.415
	{ .1838	311.25	3.416
B.	{ .1892	318.75	3.398
	{ .1806	305.28	3.409
	{ .2026	333.81	3.404
C.	.1933	325.93	3.401
D.	{ .1890	319.77	3.412
	{ .1942	328.15	3.408
	{ .1781	301.09	3.410
			Mean, 3.411, $\pm .001$

*Cobalt.*

	<i>Wt. Co.</i>	<i>Vol. H in cc.</i>	<i>Ratio.</i>
A.	{ .1958	321.36	3.395
	{ .1905	312.95	3.398
	{ .1946	319.63	3.397
	{ .2002	328.96	3.398
B.	{ .1996	328.43	3.403
	{ .2000	329.55	3.401
	{ .1721	290.17	3.401
C.	{ .1877	308.97	3.404
	{ .1935	318.60	3.405
D.	{ .1909	314.73	3.410
	{ .1834	305.40	3.407
			Mean, 3.4017, $\pm .0009$

The weight of the hydrogen in these determinations was doubtless computed from Regnault's data concerning the density of that gas. Correcting by the new value for the weight of a litre of hydrogen, .089872 gramme, the ratios become:

For nickel .....	3.4211, $\pm .0010$
For cobalt ..	3.4112, $\pm .0009$

Some time after the publication of Russell's first paper, but before the appearance of his second, some other investigations were made known.

Of these the first was by Sommaruga,\* whose results, obtained by novel methods, closely confirmed those of Schneider and antagonized those of Dumas, Marignac, and Russell. The atomic weight of nickel Sommaruga deduced from analyses of the nickel potassium sulphate,  $K_2Ni(SO_4)_2 \cdot 6H_2O$ , which, dried at  $100^\circ$ , has a perfectly definite composition. In this salt the sulphuric acid was determined in the usual way as barium sulphate, a process to which there are obvious objections. In the third column are given the quantities of the nickel salt proportional to 100 parts of  $BaSO_4$ :

0.9798	gram.	gave	1.0462	gram.	$BaSO_4$ .	93.653
1.0537	"		1.1251	"		93.654
1.0802	"		1.1535	"		93.645
1.1865	"		1.2669	"		93.654
3.2100	"		3.4277	"		93.649
3.2124	"		3.4303	"		93.648

Mean, 93.6505,  $\pm .001$

For cobalt Sommaruga used the purpureocobalt chloride of Gibbs and Genth. This salt, dried at  $110^\circ$ , is anhydrous and stable. Heated hotter,  $CoCl_2$  remains. The latter, ignited in hydrogen, yields metallic cobalt. In every experiment the preliminary heating must be carried on cautiously until ammoniacal fumes no longer appear:

.6656	gram.	gave	.1588	gram.	Co.	23.858	per cent.
1.0918	"		.2600	"		23.814	"
.9058	"		.2160	"		23.846	"
1.5895	"		.3785	"		23.813	"
2.9167	"		.6957	"		23.847	"
1.8390	"		.4378	"		23.806	"
2.5010	"		.5968	"		23.808	"

Mean, 23.827,  $\pm .006$

Further along this series will be combined with a similar one by Lee. It may here be said that Sommaruga's paper was quickly followed by a critical essay from Schneider,† endorsing the former's work and objecting to the results of Russell.

In 1867 still another new process for the estimation of these atomic weights was put forward by Winkler,‡ who determined the amount of gold which pure metallic nickel and cobalt could precipitate from a neutral solution of sodio-auric chloride.

In order to obtain pure cobalt Winkler prepared purpureocobalt chloride, which, having been four or five times recrystallized, was ignited in hydrogen. His nickel was repeatedly purified by precipitation with sodium hypochlorite. From material thus obtained pure nickel chloride

\* Sitzungsab. Wien. Akad., 54, 2 Abth., 50. 1866.

† Poggend. Annalen, 130, 310.

‡ Zeit. Anal. Chem., 6, 18. 1867.

was prepared, which, after sublimation in dry chlorine, was also reduced by hydrogen. One hundred parts of gold are precipitated by the quantities of nickel and cobalt given in the third columns respectively. In the cobalt series I include one experiment by Weselsky, which was published by him in a paper presently to be cited:

.4360	gram. nickel precipitated	.9648	gram. gold,	45.191
.4367	"	.9666	"	45.179
.5189	"	1.1457	"	45.291
.6002	"	1.3286	"	45.175
				Mean, 45.209, $\pm .019$
.5890	gram. cobalt precipitated	1.3045	gram. gold,	45.151
.3147	"	.6981	"	45.080
.5829	"	1.2913	"	45.141
.5111	"	1.1312	"	45.182
.5821	"	1.2848	"	45.307
.559	"	1.241	"	45.044—Weselsky.
				Mean, 45.151, $\pm .025$

Weselsky's paper,\* already quoted, relates only to cobalt. He ignited the cobaltcyanides of ammonium and of phenylammonium in hydrogen, and from the determinations of cobalt thus made deduced its atomic weight. His results are as follows:

.7575	gram. $(\text{NH}_4)_6\text{Co}_2\text{Cy}_{12}$ gave	.166	gram. Co.	21.914	per cent.
.5143	"	.113	"	21.972	"
				Mean, 21.943, $\pm .029$	
.8529	gram. $(\text{C}_6\text{H}_5\text{N})_6\text{Co}_2\text{Cy}_{12}$ gave	.1010	gram. Co.	11.842	per cent.
.6112	"	.0723	"	11.829	"
.7140	"	.0850	"	11.905	"
.9420	"	.1120	"	11.890	"
				Mean, 11.8665, $\pm .0124$	

Next in order is the work done by Lee† in the laboratory of Wolcott Gibbs. Like Weselsky, Lee ignited certain cobaltcyanides and also nickelocyanides in hydrogen and determined the residual metal. The double cyanides chosen were those of strychnia and brucia, salts of very high molecular weight, in which the percentages of metal are relatively low. A series of experiments with purpureocobalt chloride was also carried out. In order to avoid admixture of carbon in the metallic residues, the salts were first ignited in air, and then in oxygen. Reduction by hydrogen followed. The salts were in each case covered by a porous septum of earthenware, through which the hydrogen diffused, and which served to prevent the mechanical carrying away of solid particles; fur-

\* Ber. d. Deutsch. Chem. Gesell., 2, 592. 1868.

† Am. Journ. Sci. and Arts (3), 2, 44. 1871.

thermore, heat was applied from above. The results attained were very satisfactory, and assign to nickel and cobalt atomic weights varying from each other by about a unit; Ni being nearly 58, and Co about 59, when  $O = 16$ . The exact figures will appear later. The cobalt results agree remarkably well with those of Weselsky. The following are the data obtained:

*Brucia nickelocyanide*,  $Ni_3Cy_{12}(C_{23}H_{26}N_2O_4)_6H_6 \cdot 10H_2O$ .

<i>Salt.</i>	<i>Ni.</i>	<i>Per cent. Ni.</i>
.3966	.0227	5.724
.5638	.0323	5.729
.4000	.0230	5.750
.3131	.01795	5.733
.4412	.0252	5.712
.4346	.0249	5.729

Mean, 5.7295,  $\pm .0034$

*Strychnia nickelocyanide*,  $Ni_3Cy_{12}(C_{21}H_{22}N_2O_2)_6H_6 \cdot 8H_2O$ .

<i>Salt.</i>	<i>Ni.</i>	<i>Per cent. Ni.</i>
.5358	.0354	6.607
.5489	.0363	6.613
.3551	.0234	6.589
.4495	.0297	6.607
.2530	.0166	6.561
.1956	.0129	6.595

Mean, 6.595,  $\pm .005$

*Brucia cobalticyanide*,  $Co_2Cy_{12}(C_{23}H_{26}N_2O_4)_6H_6 \cdot 20H_2O$ .

<i>Salt.</i>	<i>Co.</i>	<i>Per cent. Co.</i>
.4097	.0154	3.759
.3951	.0147	3.720
.5456	.0204	3.739
.4402	.0165	3.748
.4644	.0174	3.747
.4027	.0151	3.749

Mean, 3.7437,  $\pm .0036$

*Strychnia cobalticyanide*,  $Co_2Cy_{12}(C_{21}H_{22}N_2O_2)_6H_6 \cdot 8H_2O$ .

<i>Salt.</i>	<i>Co.</i>	<i>Per cent. Co.</i>
.4255	.0195	4.583
.4025	.0185	4.596
.3733	.0170	4.554
.4535	.0207	4.564
.2753	.0126	4.577
.1429	.0065	4.549

Mean, 4.5705,  $\pm .005$

*Purpureo-cobalt chloride,  $\text{Co}_2(\text{NH}_3)_{10}\text{Cl}_6$ .*

<i>Salt.</i>	<i>Co.</i>	<i>Per cent. Co.</i>
.9472	.2233	23.575
.8903	.2100	23.587
.6084	.1435	23.586
.6561	.1547	23.579
.6988	.1647	23.569
.7010	.1653	23.581

Mean, 23.5795,  $\pm .0019$

The last series may be combined with Sommaruga's, thus :

Sommaruga.....	23.817, $\pm .006$
Lee .....	23.5795, $\pm .0019$
General mean.....	23.6045, $\pm .0018$

Baubigny's\* determinations of the atomic weight of nickel are limited to two experiments upon the calcination of nickel sulphate, and his data are as follows :

6.2605 grm. $\text{NiSO}_4$ gave 3.0225 $\text{NiO}$ .	48.279 per cent.
4.4935           "           2.1695   "	48.281   "

Mean, 48.280

Zimmermann's work, published after his death by Krüss and Alibegoff,† was based, like Russell's, upon the reduction of cobalt and nickel oxides in hydrogen. The materials used were purified with great care, and the results were as follows :

*Nickel.*

<i>NiO.</i>	<i>Ni.</i>	<i>Per cent. Ni.</i>
6.0041	4.7179	78.578
6.4562	5.0734	78.582
8.5960	6.7552	78.585
4.7206	3.7096	78.583
8.2120	6.4536	78.587
9.1349	7.1787	78.585
10.0156	7.8702	78.579
4.6482	3.6526	78.580
8.9315	7.0184	78.580
10.7144	8.4196	78.582
3.0036	2.3602	78.579

Mean, 78.582,  $\pm .0006$

\* Compt. Rend., 97, 951. 1883.

† Ann. der Chem., 232, 324. 1886.



*Cobalt.*

<i>CoO.</i>	<i>Co.</i>	<i>Per cent. Co.</i>
6.3947	5.0284	78.634
6.6763	5.2501	78.638
5.6668	4.4560	78.633
2.9977	2.3573	78.637
8.7446	6.8763	78.635
3.2625	2.5655	78.636
6.3948	5.0282	78.630
8.2156	6.4606	78.638
9.4842	7.4580	78.636
9.9998	7.8630	78.632

Mean, 78.635,  $\pm$  .0002

Shortly after the discovery of nickel carbonyl,  $\text{NiC}_4\text{O}_4$ , Mond, Langer, and Quincke\* made use of it with reference to the atomic weight of nickel. The latter was purified by distillation as nickel carbonyl, then converted into oxide, and that was reduced by hydrogen in the usual way.

<i>NiO.</i>	<i>Ni.</i>	<i>Per cent. Ni.</i>
.2414	.1896	78.542
.3186	.2503	78.562
.3391	.2663	78.531

Mean, 78.545,  $\pm$  .0061

Schutzenberger's experiments,† published in 1892, were also few in number. First, nickel sulphate, dehydrated at  $440^\circ$ , was calcined to oxide.

3.505	gram. $\text{NiSO}_4$ gave 1.690	$\text{NiO}$ .	48.217	per cent.
2.6008	"	1.2561	"	48.297

Mean, 48.257,  $\pm$  .027

Second, nickel oxide was reduced in hydrogen, as follows:

1.6865	gram. $\text{NiO}$ gave 1.3245	$\text{Ni}$ .	78.535	per cent.
1.2527	"	.9838	"	78.533

Mean, 78.534

In one experiment with cobalt oxide, 3.491 gram. gave 2.757 Co, or 78.975 per cent. In view of the many determinations of this ratio by other observers, this single estimation may be neglected. The experiments on nickel sulphate, however, should be combined with those of Marignac and Baubigny, giving the latter equal weight with Schutzenberger's, thus:

\* Journ. Chem. Soc., 57, 753. 1890.

† Compt. Rend., 114, 1149. 1892.

Marignac.....	48.287, $\pm$ .0675
Baubigny.....	48.280, $\pm$ .027
Schutzenberger....	48.257, $\pm$ .027
General mean....	48.269, $\pm$ .018

From this point on the determination of these atomic weights is complicated by the questions raised by Krüss as to the truly elementary character of nickel and cobalt. If that which has been called nickel really contains an admixture of some other hitherto unknown element, then all the determinations made so far are worthless, and the investigations now to be considered bear directly upon that question. First in order comes Remmler's research upon cobalt.\* This chemist, asking whether cobalt is homogeneous, prepared cobaltic hydroxide in large quantity, and made a series of successive ammoniacal extracts from it, twenty-five in all. Each extract represented a fraction, from which, by a long series of operations, cobalt monoxide was prepared, and the latter was reduced in hydrogen after the manner of Russell. The actual determinations began with the second fraction, and the data are subjoined, the number of the fraction being given with each experiment:

	<i>CoO.</i>	<i>Co.</i>	<i>Per cent. Co.</i>
2.....	.09938	.07837	78.859
3.....	.15021	.11814	78.650
4.....	.22062	.17360	78.687
5.....	.39011	.30681	78.647
6.....	.28820	.22661	78.629
7.....	.34304	.26968	78.615
8.....	.43703	.34321	78.532
9.....	.91477	.71864	78.560
10.....	.63256	.49661	78.508
11.....	.32728	.25701	78.529
12.....	.38042	.29899	78.595
13.....	.16580	.13027	78.571
14.....	1.01607	.79873	78.610
15.....	1.31635	1.03545	78.661
16.....	.91945	.72315	78.650
17.....	.53100	.41773	78.668
18.....	.82381	.64728	78.572
19.....	.81139	.63754	78.574
20.....	.76698	.60292	78.610
21.....	1.13693	.89412	78.643
22.....	2.00259	1.57495	78.646
23.....	1.04629	.82185	78.549
24.....	.48954	.38466	78.576
25.....	.69152	.54326	78.560

Mean, 78.613,  $\pm$  .0099

\* Zeit. Anorg. Chem., 2, 221. Also more fully in an Inaugural Dissertation, Erlangen, 1891.

Considered with reference to the purpose of the investigation, this mean and its probable error have no real significance. But it is very close to the means of other experimenters, and a study of the variations represented by the several fractions seems to indicate fortuity rather than system. Remmler regards his results as indicating lack of homogeneity in his material; but it seems more probable that such differences as exist are due to experimental errors and to impurities acquired in the long process of purification to which each fraction was submitted, rather than to any uncertainty regarding the nature of cobalt itself. For either interpretation the data are inconclusive, and I therefore feel justified in treating the mean like other means, and in combining it finally with them.

From the same point of view—that is, with reference to the supposed heterogeneity of nickel—Krüss and Schmidt\* carried out a series of fractionations of the metal by distillation in a stream of carbon monoxide. Nickel oxide, free from obnoxious impurities, was first reduced to metal by heating in hydrogen, after which the current of carbon monoxide was allowed to flow. The latter, carrying its small charge of nickel tetracarbonyl was then passed through a Winkler's absorption apparatus containing pure aqua regia, from which, by evaporation, nickel chloride was obtained, and from that, by reduction in hydrogen, the nickel. Ten such fractions were successively prepared and studied; first, by preparation of NiO and its reduction in hydrogen; and, secondly, in some cases, by the reoxidation of the reduced metal, so as to give a synthetic value for the ratio Ni:O. The data obtained are as follows, the successive fractions being numbered:

*Reduction of NiO.*

	<i>NiO.</i>	<i>Ni.</i>	<i>Per cent. Ni.</i>
1. {	.3722	.2926	78.614
	.7471	.5870	78.571
2. {	.7659	.60085	78.450
	.7606	.5961	78.372
3. {	1.0175	.7984	78.467
	1.2631	.99065	78.430
	1.2582	.9868	78.429
4. {	.5193	.4076	78.490
	.9200	.7215	78.424
5. {	.4052	.3179	78.455
	.6518	.5111	78.414
6. {	.5623	.4399	78.232
	.5556	.4350	78.294
7. {	.9831	.7724	78.568
	.9765	.7646	78.300
	.9639	.7557	78.400

\* Zeit. Anorg. Chem., 2, 235. 1892.

8.	{	.5756	.4538	78.839
		.56765	.4451	78.411
		.5663	.4438	78.368
		.5449	.4272	78.400
9.	{	.3174	.2491	78.481
		.3148	.2467	78.367
10.	{	.4976	.3904	78.457
		.4961	.3891	78.432
				<hr/>
				Mean, 78.444, $\pm$ .0166

*Oxidation of Ni.*

	<i>Ni.</i>	<i>NiO.</i>	<i>Per cent. Ni.</i>
1.	.5870	.7471	78.571
2.	{	.7659	78.372
		.5961	78.359
3.	{	.7988	78.506
		.9913	78.482
		.9868	78.429
4.	{	.4093	78.818
		.7216	78.435
5.	{	.3194	78.825
		.5111	78.414
6.	{	.4415	78.517
		.4350	78.294
7.	{	.7752	78.853
		.7667	78.515
		.7558	78.411
8.	{	.4555	79.135
		.4456	78.499
		.44415	78.430
		.4423	78.394
9.	{	.2508	79.015
		.2467	78.367
10.	{	.3918	78.738
		.3891	78.432
			<hr/>
			Mean, 78.557, $\pm$

To these data of Krüss and Schmidt the remarks already made concerning Remmler's work seem also to apply. The variations appear to be fortuitous, and not systematic, although the authors seem to think that they indicate a compositeness in that substance which has been hitherto regarded as elementary nickel. There is doubtless something to be said on both sides of the question; but if Krüss and Schmidt are right, all previous atomic weight determinations for cobalt and nickel are invalidated. In view of all the evidence, therefore, I prefer to regard their varying estimations as affected by accidental errors, and to treat their means like others. On this basis, their work combines with previ-

ous work as follows, Schutzenberger's measurements of the ratio NiO: Ni being assigned equal weight with those of Mond, Langer, and Quincke:

Russell.....	78.593, $\pm$ .0018
Zimmermann.....	78.582, $\pm$ .0006
Mond, Langer, and Quincke .....	78.545, $\pm$ .0061
Schutzenberger.....	78.534, $\pm$ .0061
Krüss and Schmidt, reduction series .....	78.444, $\pm$ .0166
Krüss and Schmidt, oxidation series .....	78.557, $\pm$ .0319
General mean.....	78.570, $\pm$ .0006

In 1889 Winkler\* published a short paper concerning the gold method for determining the atomic weights in question, but gave in it no actual measurements. In 1893† he returned to the problem with a new line of attack, and at the same time he takes occasion to criticise Krüss and Schmidt somewhat severely. He utterly rejects the notion that either nickel or cobalt contain any hitherto unknown element, and ascribes the peculiar results obtained by Krüss and Schmidt to impurities derived from the glass apparatus used in their experiments. For his own part he now works with pure nickel and cobalt precipitated electrolytically upon platinum, and avoids the use of glass or porcelain vessels so far as possible. With material thus obtained he operates by two distinct but closely related methods, both starting with the metal, nickel or cobalt, converting it next into neutral chloride, and then measuring the chloride gravimetrically in one process, volumetrically in the other.

After precipitation in a platinum dish, the nickel or cobalt is washed with water, rinsed with alcohol and ether, and then weighed. It is next dissolved in pure hydrochloric acid, properly diluted, and by evaporation to dryness and long heating to 150° converted into anhydrous chloride. The nickel chloride thus obtained dissolves perfectly in water, but the cobalt salt always gave a slight residue in which the metal was electrolytically determined and allowed for. In the redissolved chloride, by precipitation with silver nitrate, silver chloride is obtained, giving a direct ratio between that compound and the nickel or cobalt originally taken. The gravimetric data are as follows, with the metal equivalent to 100 parts of silver chloride given in a final column:

*Nickel.*

<i>Ni.</i>	<i>AgCl.</i>	<i>Ratio.</i>
.3011	1.4621	20.594
.2242	1.0081	20.605
.5166	2.5108	20.570
.4879	2.3679	20.605
.3827	1.8577	20.601
.3603	1.7517	20.568

Mean, 20.590,  $\pm$ .0049

\* Ber. Deutsch. Chem. Gesell., 22, 891. 1889.

† Zeit. Anorg. Chem., 4, 10. 1893.

<i>Cobalt.</i>		
<i>Co.</i>	<i>AgCl.</i>	<i>Ratio.</i>
.3458	1.6596	20.836
.3776	1.8105	20.856
.4493	2.1521	20.877
.4488	2.1520	20.855
.2856	1.3683	20.873
.2648	1.2768	20.886

Mean, 20.864,  $\pm$  .0050

In the volumetric determinations the neutral chloride, prepared as before, was decomposed by means of a slight excess of potassium carbonate, and in the potassium chloride solution, after removal of the nickel or cobalt, the chlorine was measured by titration by Volhard's method with a standard solution of silver. The amount of silver thus used was comparable with the metal taken.

<i>Nickel.</i>		
<i>Ni.</i>	<i>Ag.</i>	<i>Ratio.</i>
.1812	.6621260	27.366
.1662	.6079206	27.339
.2129	.7775252	27.382
.2232	.8162108	27.346
.5082	1.8556645	27.386
.1453	.5315040	27.338

Mean, 27.359,  $\pm$  .0059

<i>Cobalt.</i>		
<i>Co.</i>	<i>Ag.</i>	<i>Ratio.</i>
.177804	.6418284	27.702
.263538	.9514642	27.699
.245124	.8855780	27.679
.190476	.6866321	27.741
.266706	.9629146	27.696
.263538	.9503558	27.731

Mean, 27.708,  $\pm$  .0064

In view of the possibility that the cobalt chloride of the foregoing experiments might contain traces of basic salt, Winkler, in a supplementary investigation,\* checked them by another process. To the electrolytic cobalt, in a platinum dish, he added a quantity of neutral silver sulphate and then water. The cobalt gradually went into solution, and metallic silver was precipitated. The weights were as follows:

<i>Co.</i>	<i>Ag.</i>
.2549	.9187
.4069	1.4691

\* Zeit. Anorg. Chem., 4, 462. 1893.

On examination of the silver it was found that traces of cobalt were retained—less than 0.5 mg. in the first determination and less than 0.2 mg. in the second. Taking these amounts as corrections, the two experiments give for the ratios  $\text{Ag}_2 : \text{Co} :: 100 : x$  the subjoined values :

$$\begin{array}{c} 27.706 \\ 27.687 \end{array}$$

These figures confirm those previously found, and as they fall within the limits of the preceding series, they may fairly be included in it, when all eight values give a mean of  $27.705, \pm .0050$ .

Still another method, radically different from all of the foregoing processes, was adopted by Winkler in 1894.\* The metals were thrown down electrolytically upon platinum, and so weighed. Then they were treated with a known excess of a decinormal solution of iodine in potassium iodide, which redissolved them as iodides. The excess of free iodine was then determined by titration with sodium thiosulphate, and in that way the direct ratio between metal and haloid was ascertained. The results were as follows, with the metal proportional to 100 parts of iodine given in the third column :

*Cobalt.*

	<i>Wt. Co.</i>	<i>Wt. I.</i>	<i>Ratio.</i>
First series . . . .	.4999	2.128837	23.482
	.5084	2.166750	23.463
	.5290	2.254335	23.466
	.6822	2.908399	23.456
	.6715	2.861617	23.466
Second series. .	.5185	2.209694	23.465
	.5267	2.246037	23.450
	.5319	2.268736	23.445
			Mean, 23.462, $\pm .0027$

*Nickel.*

	<i>Wt. Ni.</i>	<i>Wt. I.</i>	<i>Ratio.</i>
First series. . . .	.5144	2.217494	23.251
	.4983	2.148502	23.246
	.5265	2.268742	23.260
	.6889	2.970709	23.243
	.6876	2.965918	23.237
Second series. .	.5120	2.205627	23.267
	.5200	2.240107	23.267
	.5246	2.259925	23.267
			Mean, 23.255, $\pm .0091$

In these experiments, as well as in some previous series, a possible source of error is to be considered in the occlusion of hydrogen by the

\* Zeitsch. Anorg. Chem., 8, 1. 1894.

metals. Accordingly, in a supplementary paper, Winkler\* gives the results of some check experiments made with iron, which, however, was not absolutely pure. The conclusion is that the error, if existent, must be very small.

In 1895 Hempel and Thiele's work on cobalt appeared.† First, cobalt oxide, prepared from carefully purified materials, was reduced in hydrogen. The weights of metal and oxygen are subjoined, with the percentage of cobalt in the oxide deduced from them :

<i>Co.</i>	<i>O.</i>	<i>Percentage.</i>
.90068	.24429	78.664
.79159	.21445	78.686
1.31558	.35716	78.648
		<hr/>
		Mean, 78.666, $\pm .0074$

This mean combines with former means as follows :

Russell.....	78.592, $\pm .0023$
Zimmermann.....	78.635, $\pm .0002$
Remmler.....	78.613, $\pm .0099$
Hempel and Thiele.....	78.666, $\pm .0074$
<hr/>	
General mean.....	78.633, $\pm .0002$

In their next series of experiments, excluding a rejected series, Hempel and Thiele weighed cobalt, converted it into anhydrous chloride, and noted the gain in weight. In four of the experiments the chloride was afterwards dissolved, precipitated with silver nitrate, and then the silver chloride was weighed. The data are as follows :

<i>Co.</i>	<i>Cl Taken Up.</i>	<i>AgCl.</i>
.7010	.8453	.....
.3138	.3793	.....
.2949	.3562	1.4340
.4691	.5657	2.2812
.5818	.7026	2.8303
.5763	.6947	.....
.5096	.6142	2.4813

From these weights we get two ratios, thus :

<i>Cl<sub>2</sub> : Co : 100 : x.</i>	<i>2AgCl : Co : 100 : x.</i>
82.929	20.565
82.731	20.564
82.791	20.556
82.924	20.538
82.807	<hr/>
82.957	Mean, 20.556, $\pm .0043$
82.970	
<hr/>	
Mean, 82.873, $\pm .0241$	

\* Zeitsch. Anorg. Chem., 8, 291. 1895.

† Zeitsch. Anorg. Chem., 11, 73.



The second of these ratios was also studied by Winkler, and the two series combine as follows:

Winkler.....	20.864, $\pm$ .0050
Hempel and Thiele.....	20.556, $\pm$ .0043
General mean.....	20.687, $\pm$ .0033

Hempel and Thiele apply to it a correction for silver chloride retained in solution, but its amount is small and not altogether certain. For present purposes the correction may be neglected.

For the atomic weight of nickel we now have ratios as follows:

- (1.) Per cent. of Ni in  $\text{NiC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ , 29.084,  $\pm$  .006
- (2.) Per cent. of  $\text{CO}_2$  from  $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , 44.098,  $\pm$  .027
- (3.) Per cent. of Ni in  $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , 31.408,  $\pm$  .0026
- (4.) Per cent. of  $\text{CO}_2$  from  $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , 47.605,  $\pm$  .053
- (5.) Per cent. of Ni in brucia nickelocyanide, 5.7295,  $\pm$  .0034
- (6.) Per cent. of Ni in strychnia nickelocyanide, 6.595,  $\pm$  .005
- (7.) Per cent. of NiO in  $\text{NiSO}_4$ , 48.269,  $\pm$  .018
- (8.) Per cent. of Ni in NiO, 78.570,  $\pm$  .0006
- (9.)  $\text{Ag}_2 : \text{NiCl}_2 :: 100 : 60.194$ ,  $\pm$  .0061
- (10.)  $2\text{AgCl} : \text{Ni} :: 100 : 20.590$ ,  $\pm$  .0049
- (11.)  $\text{Ag}_2 : \text{Ni} :: 100 : 27.359$ ,  $\pm$  .0059
- (12.)  $\text{Au}_2 : \text{Ni}_3 :: 100 : 45.209$ ,  $\pm$  .019
- (13.)  $\text{BaSO}_4 : \text{K}_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O} :: 100 : 93.6505$ ,  $\pm$  .001
- (14.)  $\text{Ni} : \text{H}_2 :: 100 : 3.4211$ ,  $\pm$  .001
- (15.)  $\text{I}_2 : \text{Ni} :: 100 : 23.255$ ,  $\pm$  .0091

To the reduction of these ratios the following atomic and molecular weights are applicable:

O = 15.879, $\pm$ .0003	I = 125.888, $\pm$ .0069
C = 11.920, $\pm$ .0004	K = 38.817, $\pm$ .0051
N = 13.935, $\pm$ .0021	Ba = 136.392, $\pm$ .0086
S = 31.828, $\pm$ .0035	Au = 195.743, $\pm$ .0049
Ag = 107.108, $\pm$ .0031	AgCl = 142.287, $\pm$ .0037
Cl = 35.179, $\pm$ .0048	

Since the proportion of water in the oxalates is not an absolutely certain quantity, the data concerning them can be best handled by employing the ratios between carbon dioxide and the metal. Accordingly, ratios (1) and (2) give a single value for Ni, and ratios (3) and (4) another. In all, there are thirteen values for the atomic weight in question:

From (1) and (2).....	Ni = 57.614, $\pm$ .0372
From (5).....	" = 57.625, $\pm$ .0343
From (3) and (4).....	" = 57.635, $\pm$ .0644
From (6).....	" = 57.687, $\pm$ .0439
From (8).....	" = 58.218, $\pm$ .0020
From (7).....	" = 58.268, $\pm$ .0428
From (13).....	" = 58.448, $\pm$ .0206

From (14). . . . .	Ni = 58.456, $\pm$ .0316
From (15) . . . . .	" = 58.551, $\pm$ .0231
From (9) . . . . .	" = 58.587, $\pm$ .0179
From (10) . . . . .	" = 58.594, $\pm$ .0141
From (11) . . . . .	" = 58.607, $\pm$ .0128
From (12) . . . . .	" = 58.994, $\pm$ .0248
<hr/>	
General mean . . . . .	Ni = 58.243, $\pm$ .0019

If O = 16, this becomes Ni = 58.687.

It is quite evident here that ratio (8), which includes the marvelously concordant determinations of Zimmermann, far outweighs all the other data. Whether so excessive a weight can justifiably be assigned to one set of measurements is questionable, but the general mean thus reached is not far from midway between the highest and lowest of the values, and hence it may fairly be entitled to provisional acceptance. No one of the individual values rests upon absolutely conclusive evidence, so that no one can be arbitrarily chosen to the exclusion of the others. Further investigation is evidently necessary.

For cobalt we have sixteen ratios, as follows :

- (1.) Per cent. of Co in  $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , 32.5555,  $\pm$ .0149
- (2.) Per cent. of  $\text{CO}_2$  from  $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , 47.7475,  $\pm$ .0213
- (3.) Per cent. of Co in CoO, 78.633,  $\pm$ .0002
- (4.) Per cent. of Co in purplecobalt chloride, 23.6045,  $\pm$ .0018
- (5.) Per cent. of Co in phenylammonium cobalticyanide, 11.8665,  $\pm$ .0124
- (6.) Per cent. of Co in ammonium cobalticyanide, 21.943,  $\pm$ .029
- (7.) Per cent. of Co in brucia cobalticyanide, 3.7437,  $\pm$ .0036
- (8.) Per cent. of Co in strychnia cobalticyanide, 4.5705,  $\pm$ .005
- (9.) Per cent. of CoO in  $\text{CoSO}_4$ , 48.287,  $\pm$ .0135
- (10.)  $\text{Ag}_2 : \text{CoCl}_2 :: 100 : 60.200$ ,  $\pm$ .0095
- (11.)  $2\text{AgCl} : \text{Co} :: 100 : 20.687$ ,  $\pm$ .0033
- (12.)  $\text{Ag}_2 : \text{Co} :: 100 : 27.705$ ,  $\pm$ .0050
- (13.)  $\text{Au}_2 : \text{Co}_3 :: 100 : 45.151$ ,  $\pm$ .025
- (14.)  $\text{Co} : \text{H}_2 :: 100 : 3.4110$ ,  $\pm$ .0009
- (15.)  $\text{I}_2 : \text{Co} :: 100 : 23.462$ ,  $\pm$ .0027
- (16.)  $\text{Cl}_2 : \text{Co} :: 100 : 82.873$ ,  $\pm$ .0241

From these, using the atomic weights already cited under nickel, and combining ratios (1) and (2), we get—

From (16) . . . . .	Co = 58.308, $\pm$ .0187
From (9) . . . . .	" = 58.321, $\pm$ .0288
From (3) . . . . .	" = 58.437, $\pm$ .0014
From (10) . . . . .	" = 58.600, $\pm$ .0228
From (14) . . . . .	" = 58.630, $\pm$ .0286
From (5) . . . . .	" = 58.639, $\pm$ .0619
From (8) . . . . .	" = 58.696, $\pm$ .0642
From (6) . . . . .	" = 58.736, $\pm$ .0808
From (4) . . . . .	" = 58.774, $\pm$ .0071
From (7) . . . . .	" = 58.791, $\pm$ .0566

From (11).....	Co = 58.870, $\pm$ .0094
From (13).....	" = 58.920, $\pm$ .0327
From (15).....	" = 59.072, $\pm$ .0075
From (12).....	" = 59.349, $\pm$ .0108
From (1) and (2).....	" = 59.562, $\pm$ .0382
<hr/>	
General mean.....	Co = 58.487, $\pm$ .0013

If O = 16, this becomes Co = 58.932.

Here again the oxide ratio, because of Zimmermann's work, receives excessive and undue weight. The arithmetical mean of the fifteen values is Co = 58.781. Between this and the weighted general mean the truth probably lies, but the evidence is incomplete, and more determinations are needed.

## RUTHENIUM.

The atomic weight of this metal has been determined by Claus and by Joly. Although Claus\* employed several methods, we need only consider his analyses of potassium rutheniochloride,  $K_2RuCl_3$ . The salt was dried by heating to 200° in chlorine gas, but even then retained a trace of water. The percentage results of the analyses are as follows:

<i>Ru.</i>	<i>2KCl.</i>	<i>Cl<sub>3</sub>.</i>
28.96	40.80	30.24
28.48	41.39	30.22
28.91	41.08	30.04
<hr/>		<hr/>
Mean, 28.78	41.09	30.17

Reckoning directly from the percentages, we get the following discordant values for Ru:

From percentage of metal .....	Ru = 102.451
From percentage of KCl .....	" = 106.778
From percentage of Cl <sub>3</sub> .....	" = 96.269

These results are obviously of little importance, especially since the best of them is not in accord with the position of ruthenium in the periodic system. The work of Joly is more satisfactory.† Several compounds of ruthenium were analyzed by reduction in a stream of hydrogen with the following results:

\* Journ. für Prakt. Chem., 34, 435. 1845.

† Compt. Rend., 108, 946.

First, reduction of  $\text{RuO}_2$ :

$\text{RuO}_2$ .	$\text{Ru}$ .	<i>Per cent. Ru.</i>
2.1387	1.6267	76.060
2.5846	1.9658	76.058
2.3682	1.8016	76.075
2.8849	2.1939	<u>76.046</u>
		Mean, 76.060, $\pm .0040$

Second, reduction of the salt  $\text{RuCl}_3 \cdot \text{NO} \cdot \text{H}_2\text{O}$ :

<i>Per cent. Ru.</i>
39.78
<u>39.66</u>
Mean, 39.72, $\pm .0405$

Third, reduction of  $\text{RuCl}_3 \cdot \text{NO} \cdot 2\text{NH}_4\text{Cl}$ :

<i>Per cent. Ru.</i>
29.44
<u>29.47</u>
Mean, 29.455, $\pm .0101$

Computing with  $\text{O} = 15.879, \pm .0003$ ;  $\text{N} = 13.935, \pm .0021$ , and  $\text{Cl} = 35.179, \pm .0048$ , these data give three values for ruthenium, as follows:

1. From $\text{RuO}_2$ .....	$\text{Ru} = 100.922, \pm .0178$
2. From $\text{RuCl}_3 \cdot \text{NO} \cdot \text{H}_2\text{O}$ .....	" = $100.967, \pm .1102$
3. From $\text{RuCl}_3 \cdot \text{NO} \cdot 2\text{AmCl}$ .....	" = $100.868, \pm .0387$
General mean .....	<u><math>\text{Ru} = 100.913, \pm .0160</math></u>

If  $\text{O} = 16$ ,  $\text{Ru} = 101.682$ .

## RHODIUM.

Berzelius\* determined the atomic weight of this metal by the analysis of sodium and potassium rhodochlorides,  $\text{Na}_3\text{RhCl}_6$ , and  $\text{K}_2\text{RhCl}_5$ . The latter salt was dried by heating in chlorine. The compounds were analyzed by reduction in hydrogen, after the usual manner. Reduced to percentages, the analyses are as follows :

*In  $\text{Na}_3\text{RhCl}_6$ .*

<i>Rh.</i>	<i>3NaCl.</i>	<i>Cl<sub>3</sub>.</i>
26.959	45.853	27.189
27.229	45.301	27.470
.....	.....	27.616
<u>Mean, 27.094</u>	<u>Mean, 45.577</u>	<u>Mean, 27.425</u>

*In  $\text{K}_2\text{RhCl}_5$ .*

<i>Rh.</i>	<i>2KCl.</i>	<i>Cl<sub>3</sub>.</i>
28.989	41.450	29.561

From the analyses of the sodium salt we get the following values for Rh :

From per cent. of metal.....	Rh = 104.191
From per cent. of NaCl.....	" = 102.449
From per cent. of Cl <sub>3</sub> .....	" = 105.103
From ratio between Cl <sub>3</sub> and Rh.....	" = 104.263
From ratio between NaCl and Rh.....	" = 103.544

These are discordant figures ; but the last one fits in fairly well with the values calculated from the potassium compound, which are as follows :

From per cent. of metal.....	Rh = 103.499
From per cent. of KCl.....	" = 103.648
From per cent. of Cl <sub>3</sub> .....	" = 103.485
From Rh : Cl <sub>3</sub> ratio.....	" = 103.495
From Rh : KCl ratio.....	" = 103.540
<u>Mean.....</u>	<u>Rh = 103.533</u>

If O = 16, this becomes Rh = 104.323.

Jørgensen's determination,† so far as I can ascertain, was published only as a preliminary note, to the effect that the atomic weight of rhodium is 103, nearly. No details are given.

\* Poggend. Annalen, 13, 435. 1828.

† Journ. für Prakt. Chem. (2), 27, 486.

Seubert and Kobbe\* determine the atomic weight by igniting rhodium pentamine chloride in hydrogen, and weighing the residual metal. Their results are given below :

$Rh(NH_3)_5Cl_3$ .	<i>Rh.</i>	<i>Per cent. Rh.</i>
1.8585	.6496	34.953
1.5560	.5435	34.929
1.5202	.5310	34.930
2.0111	.7031	34.961
1.8674	.6528	34.958
2.4347	.8513	34.965
2.3849	.8338	34.962
2.5393	.8881	34.974
1.4080	.4920	34.943
1.4654	.5123	34.960

Mean, 34.954,  $\pm .0032$

In the sixth experiment the ammonium chloride formed was collected in a bulb tube, and estimated by weighing as silver chloride. 3.5531 grms. of AgCl were obtained.

Computing with  $N = 13.935, \pm .0021$ ;  $Cl = 35.179, \pm .0048$ , and  $AgCl = 142.287, \pm .0037$ , we have—

From per cent. of metal.....	Rh = 102.215, $\pm .0143$
From AgCl ratio.....	“ = 102.287, $\pm .0324$
General mean .....	Rh = 102.227, $\pm .0131$

If  $O = 16$ ,  $Rh = 103.006$ .

In the second of these values the probable error given is only that due to the antecedent atomic weights of N, Cl, and AgCl. It is therefore lower than it should be. The two values, however, are fairly in agreement, and the result is satisfactory.

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\* Ann. d. Chem., 260, 318. 1890.

## PALLADIUM.

The first work upon the atomic weight of palladium seems to have been done by Berzelius. In an early paper\* he states that 100 parts of the metal united with 28.15 of sulphur. Hence  $\text{Pd} = 113.06$ , a result which is clearly of no present value.

In a later paper † Berzelius published two analyses of potassium palladiochloride,  $\text{K}_2\text{PdCl}_4$ . The salt was decomposed by ignition in hydrogen, as was the case with the double chlorides of potassium with platinum, osmium, and iridium. Reducing his results to percentages, we get the following composition for the substance in question :

<i>Pd.</i>	<i>2KCl.</i>	<i>Cl<sub>2</sub>.</i>
32.726	46.044	21.229
<u>32.655</u>	<u>45.741</u>	<u>21.604</u>
Mean, 32.690	Mean, 45.892	Mean, 21.416

From these percentages, calculating directly, very discordant results are obtained :

From percentage of metal .....	$\text{Pd} = 106.53$
From percentage of $\text{KCl}$ .....	" = 104.13
From percentage of $\text{Cl}_2$ (loss).....	" = 110.20

Obviously, the only way to get satisfactory figures is to calculate from the ratio between the  $\text{Pd}$  and  $2\text{KCl}$ , eliminating thus the influence of water in the salt. The two experiments give, as proportional to 100 parts of  $\text{KCl}$ , the following of  $\text{Pd}$  :

71.075
<u>71.391</u>
Mean, 71.233, $\pm .1066$

Hence  $\text{Pd} = 105.419$ .

In 1847 Quintus Icilius ‡ published a determination, which need be given only for the sake of completeness. He ignited potassium palladiochloride in hydrogen, and found the following amounts of residue. His weights are here recalculated into percentages :

64.708
64.965
<u>64.781</u>
Mean, 64.818

From this mean,  $\text{Pd} = 111.258$ . This result has no present value.

\* Poggend. Annalen, 8, 177. 1826.

† Poggend. Annalen, 13, 454. 1828.

‡ "Die Atomgewichte vom  $\text{Pd}$ ,  $\text{K}$ ,  $\text{Cl}$ ,  $\text{Ag}$ ,  $\text{C}$ , und  $\text{H}$ , nach der Methode der kleinsten Quadrate berechnet." Inaug. Diss. Göttingen, 1847. Contains no other original analyses.

In 1889 Keiser's first determinations of this constant appeared.\* Finding the potassium palladiochloride to contain "water of decrepitation," he abandoned its use, and resorted to palladiumammonium chloride,  $\text{Pd}(\text{NH}_3\text{Cl})_2$ , as the most available compound for his purpose. This salt, heated in hydrogen, yields spongy palladium, which was allowed to cool in a current of dry air, in order to avoid gaseous occlusions. The salt itself was dried, previous to analysis, first over sulphuric acid, and then in an air bath at a temperature from  $120^\circ$  to  $130^\circ$ . Two series of experiments were made, the second series starting out from palladium produced by the first series. The data are as follows:

*First Series.*

$\text{Pd}(\text{NH}_3\text{Cl})_2$ .	<i>Pd.</i>	<i>Per cent. Pd.</i>
.83260	.41965	50.402
1.72635	.86992	50.391
1.40280	.70670	50.378
1.57940	.79562	50.375
1.89895	.95650	50.370
1.48065	.74570	50.363
1.56015	.78585	50.370
1.82658	.92003	50.369
2.40125	1.20970	50.378
1.10400	.55629	50.389
.93310	.47010	50.380

Mean, 50.379,  $\pm .0008$

Reduced to vacuum this becomes 50.360.

*Second Series.*

$\text{Pd}(\text{NH}_3\text{Cl})_2$ .	<i>Pd.</i>	<i>Per cent. Pd.</i>
2.61841	1.31900	50.374
2.23420	1.12561	50.381
1.73553	.87445	50.385
1.69160	.85210	50.372
1.72403	.86825	50.362
1.12222	.56535	50.378
1.17457	.59200	50.401
2.42760	1.22280	50.371

Mean, 50.378,  $\pm .0028$

Reduced to vacuum, 50.359

The reductions to vacuum are neglected by Keiser himself, but are here added in order to secure uniformity with later results by the same author. The mean of both series, thus corrected, gives  $\text{Pd} = 105.74$ .

Bailey and Lamb † made experiments upon several compounds of palladium, but finally settled upon palladiumammonium chloride, like Keiser.

\* Am. Chem. Journ., 11. 398. 1889.

† Journ. Chem. Soc., 61, 745. 1892.



Two preliminary experiments, however, with potassium palladiochloride are given, in which the salt was reduced in hydrogen, and both Pd and KCl were weighed. The data are as follows, with the ratio (calculated as with Berzelius' experiments) given in a third column :

<i>zKCl.</i>	<i>Pd.</i>	<i>Ratio.</i>
1.49767	1.05627	70.528
.90484	.63738	70.441
		<hr/>
		Mean, 70.485, $\pm .0290$

Hence Pd = 104.312.

The palladiumammonium chloride was studied by two methods. First, weighed quantities of the salt were reduced in hydrogen, the ammonium chloride so formed was collected in an absorption apparatus, and then precipitated with silver nitrate. The weights found were as follows, with the  $\text{Pd}(\text{NH}_3\text{Cl})_2$  proportional to 100 parts of silver chloride given in the third column :

<i>Pd(NH<sub>3</sub>Cl)<sub>2</sub>.</i>	<i>AgCl.</i>	<i>Ratio.</i>
1.24276	1.682249	73.879
1.08722	1.468448	74.040
1.47666	2.000164	73.828
1.34887	1.837957	73.390
1.74569	2.362320	73.898
		<hr/>
		Mean, 73.807, $\pm .0742$

Hence Pd = 105.808. Bailey and Lamb regard this as too high, and suspect loss of  $\text{NH}_4\text{Cl}$  during the operation.

The second series of data resemble Keiser's. The salt was reduced in hydrogen, and the spongy palladium was weighed in a Sprengel vacuum. The data are as follows :

	<i>Pd(NH<sub>3</sub>Cl)<sub>2</sub>.</i>	<i>Pd.</i>	<i>Per cent. Pd.</i>
A.	{ 1.890597	.947995	50.143
	{ 1.874175	.940271	50.170
B.	{ 1.307076	.654687	50.088
	{ 1.340045	.633207	50.238
	{ 1.905536	.955950	50.167
	{ 1.685582	.846472	50.218
C.	{ 1.691028	.849120	50.213
	{ 2.112530	1.059690	50.162
	{ 2.110653	1.057910	50.122
	{ 1.969100	.988155	50.184
			<hr/>
			Mean, 50.171, $\pm .0099$

Hence Pd = 104.943. Bailey and Lamb's weighings are all reduced to a vacuum.

Keller and Smith,\* reviewing Keiser's work, find that palladiummonium chloride, prepared as Keiser prepared it, may retain traces of foreign metals, and especially of copper. Accordingly, they prepared a quantity of the salt, after a thorough and elaborate process of purification, dried it with extreme care, and then determined the palladium by electrolysis in silver-coated platinum dishes. The precipitated palladium was dried under varying conditions, concerning which the original memoir must be consulted, and was proved to be free from occluded hydrogen. By this method two sets of experiments were made to determine the atomic weight of palladium; but for present purposes the two may fairly be treated as one. The data obtained are as follows, but the weights do not appear to have been reduced to a vacuum:

	$Pd(NH_3Cl)_2$ .	$Pd$ .	<i>Per cent. Pd.</i>
A.	{ 1.29960	.65630	50.504
	{ 1.05430	.53253	50.510
	{ 1.92945	.97455	50.509
B.	{ 1.94722	.98343	50.504
	{ 1.08649	.54870	50.502
	{ 1.28423	.64858	50.503
	{ 1.68275	.85010	50.519
	{ 1.69113	.85431	50.517
	{ 1.80805	.91310	50.502

Mean, 50.508,  $\pm$  .0014

Hence  $Pd = 106.368$ , a result notably higher than Keiser's.

Keller and Smith account for the difference between their determinations and Keiser's partly by the assumption that the materials used by the latter were not pure, and partly by considerations based on the process. In order to clarify the latter part of the question they made three sets of experiments by Keiser's method, slightly varying the conditions. First, the chloride was not pulverized before ignition, and slight decrepitation took place, while dark stains of palladium appeared in the reduction tube, indicating loss by volatilization. Secondly, the chloride was prepared from crude palladium exactly as described by Keiser, but was pulverized before reduction. No decrepitation ensued, but traces of palladium were volatilized. The third series, also on finely pulverized material, was like the second; but the palladiummonium chloride was purified by Keller and Smith's process. The three series, here treated as one, are as follows:

	$Pd(NH_3Cl)_2$ .	$Pd$ .	<i>Per cent. Pd.</i>
First series, . . .	{ .62955	.31743	50.422
	{ .77270	.38942	50.397
	{ .83252	.41918	50.350
	{ .99055	.49895	50.371

\* Amer. Chem. Journ., 14, 423. 1892.

	$Pd(NH_3Cl)_2$ .	$Pd$ .	<i>Per cent. Pd.</i>
Second series. . .	1.02175	.51468	50.372
	1.10325	.55590	50.388
	.66690	.33590	50.367
	.86840	.43733	50.360
	1.41430	.71255	50.382
	1.15234	.58050	50.376
Third series. . .	.96229	.48502	50.403
	.97804	.49294	50.401
	.94253	.47517	50.414
	.86090	.43405	50.430
			<hr/>
			Mean, 50.388, $\pm$ .0043

The three series seem to be fairly in agreement between themselves, and with Keiser's work, but diverge seriously from the electrolytic data.

Keller and Smith also attempted to determine the atomic weight of palladium by heating the palladiumammonium chloride in sulphuretted hydrogen, and so converting it into the sulphide, PdS. These data were obtained :

$Pd(NH_3Cl)_2$ .	$PdS$ .	<i>Per cent. CdS.</i>
.71699	.47066	65.644
1.31688	.86445	65.659
		<hr/>
		Mean, 65.651, $\pm$ .0051

Hence  $Pd = 106.55$ . This result, however, is affected by the work of Petrenko-Kritschenko,\* who has shown the existence of the sulphide PdS to be uncertain.

Joly and Leidié,† in their determinations of this atomic weight, returned to the potassium palladiochloride,  $K_2PdCl_4$ . In their first series of experiments the salt was dried in vacuo at ordinary temperatures. It was then electrolyzed in a solution acidulated with hydrochloric acid, both the deposited palladium and the potassium chloride being weighed. The palladium was dried, ignited in a stream of hydrogen, and cooled in an atmosphere of carbon dioxide. The results were as follows, with the column added by me giving the Pd equivalent to 100 parts of KCl :

$K_2PdCl_4$ .	$Pd$ .	$2KCl$ .	<i>Ratio.</i>
1.0255	.3919	.5520	70.996
1.2178	.3937	.5551	70.924
1.2518	.4048	.5687	71.016
			<hr/>
			Mean, 70.979, $\pm$ .0188

This series was rejected by the authors, because the salt was found to contain water—in one case 0.23 per cent. This error, however, should

\* Zeit. Anorg. Chem., 4, 251. 1893.

† Compt. Rend., 116, 147. 1893.

not invalidate the Pd : KCl ratio. In a second series the palladiochloride was dried in vacuo at 100°, giving the following data :

$K_2PdCl_4$ .	<i>Pd.</i>	$2KCl$ .	<i>Ratio.</i>
1.3635	.4422	.6186	71.484
3.0628	.9944	1.3929	71.391
1.4845	.4816	.6782	71.011
1.7995	.5838	.8206	71.143

Mean, 71.257,  $\pm$  .0736

These experiments seem to be less concordant than the preceding set. It must be noted, however, that the authors reject the KCl determinations and compute directly from the ratio between the salt and the metal. But the ratio here chosen agrees best with the determinations made by other observers, giving for this series the mean value Pd = 105.455, and is, moreover, uniform with the data given by Berzelius and by Bailey and Lamb.

Joly and Leidié also give two experiments made by reducing the  $K_2PdCl_4$  in hydrogen, with the subjoined results :

$K_2PdCl_4$ .	<i>Pd.</i>	$2KCl$ .	<i>Ratio.</i>
2.4481	.7949	1.1168	71.177
1.8250	.5930	.8360	70.933

Mean, 71.055,  $\pm$  .0823

Combining these data with previous series, we have—

Berzelius .....	71.233, $\pm$ .1066
Bailey and Lamb .....	70.485, $\pm$ .0290
Joly and Leidié, first .....	70.979, $\pm$ .0188
Joly and Leidié, second .....	71.257, $\pm$ .0736
Joly and Leidié, third .....	71.055, $\pm$ .0823
General mean .....	70.865, $\pm$ .0150

In view of the discordance among the determinations hitherto cited and because of the criticisms made by Keller and Smith, Keiser, jointly with Miss Mary B. Breed,\* repeated his former work, with some variations and added precautions to ensure accuracy. His general method was the same as before, namely, the reduction of palladiumammonium chloride by a stream of hydrogen. First, palladium was purified by distillation as  $PdCl_2$  at low red heat in a current of chlorine. From this chloride the palladiumammonium salt was then prepared. Upon heating the compound gently in a stream of hydrogen, decomposition ensued absolutely without decrepitation or loss of palladium by volatilization. Neither source of error existed. The results obtained were these :

\* Am. Chem. Journ., 16, 20. 1894.

$Pd(NH_3Cl)_2$ .	$Pd$ .	<i>Per cent. Pd.</i>
1.60842	.80997	50.358
2.08295	1.04920	50.371
2.02440	1.01975	50.373
2.54810	1.28360	50.375
1.75505	.88410	50.375
		<hr/>
		Mean, 50.370, $\pm .0023$
		Reduced to vacuum, 50.351

In a second series of experiments, palladium was purified as in the earlier investigation, but with special care to eliminate rhodium, iron, copper, gold, mercury, etc. The palladiumammonium salt prepared from this material gave as follows:

$Pd(NH_3Cl)_2$ .	$Pd$ .	<i>Per cent. Pd.</i>
1.50275	.75685	50.364
1.23672	.62286	50.365
1.34470	.67739	50.375
1.49059	.75095	50.379
		<hr/>
		Mean, 50.371, $\pm .0026$
		Reduced to vacuum, 50.352

Here, again, no loss from decrepitation or volatilization occurred, although evidence of such loss was carefully sought for. The data thus obtained may now be combined with the previous series, thus:

Keiser, first series.....	50.360, $\pm .0008$
Keiser, second series.....	50.359, $\pm .0028$
Bailey and Lamb.....	50.171, $\pm .0099$
Keller and Smith, electrolytic.....	50.508, $\pm .0014$
Keller and Smith, hydrogen series.....	50.388, $\pm .0043$
Keiser and Breed, first series.....	50.351, $\pm .0023$
Keiser and Breed, second series.....	50.352, $\pm .0026$
	<hr/>
General mean.....	50.388, $\pm .00062$

For palladium, ignoring the work of Quintus Icilius, the subjoined ratios are now available:

- (1.)  $2KCl : Pd :: 100 : 70.865, \pm .0150$
- (2.) Per cent. Pd in  $Pd(NH_3Cl)_2$ , 50.388,  $\pm .00062$
- (3.)  $2AgCl : Pd(NH_3Cl)_2 :: 100 : 73.807, \pm .0742$
- (4.)  $Pd(NH_3Cl)_2 : PdS :: 100 : 65.651, \pm .0051$

The antecedent data are—

Cl = 35.179, $\pm .0048$	S = 31.828, $\pm .0015$
K = 38.817, $\pm .0051$	AgCl = 142.287, $\pm .0037$
N = 13.935, $\pm .0021$	

Hence, for the atomic weight of palladium, we have—

From (1)....	Pd = 104.874, $\pm$ .0243
From (2).....	" = 105.858, $\pm$ .0200
From (3).....	" = 105.808, $\pm$ .2117
From (4).....	" = 106.550, $\pm$ .0491
<hr/>	
General mean.....	Pd = 105.556, $\pm$ .0147

With O = 16, Pd = 106.364.

Taking the values separately, the second is probably the best; but in view of the work done by Bailey and Lamb on one side, and by Keller and Smith on the other, it cannot be accepted unreservedly. Until the cause of variation in the results is clearly determined, it is better to take the general mean of all the data, as given above.

## OSMIUM.

The atomic weight of this metal has been determined by Berzelius, by Fremy, and by Seubert.

Berzelius\* analyzed potassium osmichloride, igniting it in hydrogen like the corresponding platinum salt. 1.3165 grammes lost .3805 of chlorine, and the residue consisted of .401 gm. of potassium chloride, with .535 gm. of osmium. Calculating only from the ratio between the Os and the KCl, the data give Os = 197.523.

Fremy's determination† is based upon the composition of osmium tetroxide. No details as to weighings or methods are given; barely the final result is stated. This, if O = 16, is Os = 199.648.

When the periodic law came into general acceptance, it became clearly evident that both of the foregoing values for osmium must be several units too high. A redetermination was therefore undertaken by Seubert,‡ who adopted methods based upon that of Berzelius. First, ammonium osmichloride was reduced by heating in a stream of hydrogen. The residual osmium was weighed, and the ammonium chloride and hydrochloric acid given off were collected in a suitable apparatus, so that the total chlorine could be estimated as silver chloride. The weights were as follows:

$Am_2OsCl_6$ .	Os.	$6AgCl$ .
1.8403	7996	3.5897
2.0764	.9029	4.0460
2.1501	.9344	4.1950
2.1345	.9275	4.1614

\* Poggend. Annalen, 13, 530. 1828.

† Compt. Rend., 19, 468. Journ. für Prakt. Chem., 31, 410. 1844.

‡ Berichte Deutsch. Chem. Gesell., 21, 1839. 1888.

Hence we have for the percentage of osmium and for the osmichloride proportional to 100 parts of AgCl—

<i>Per cent. Os.</i>	<i>AgCl : Salt.</i>
43.446	51.266
43.484	51.320
43.458	51.254
43.453	51.293
	<hr/>
	Mean, 51.283, $\pm .0099$

In a later paper\* two more reductions are given, in which only osmium was estimated.

<i>Salt.</i>	<i>Os.</i>	<i>Per cent. Os.</i>
2.6687	1.1597	43.456
2.6937	1.1706	43.457

These determinations, included with the previous four as one series, give a mean percentage of Os in  $\text{Am}_2\text{OsCl}_6$  of 43.459,  $\pm .0036$ .

Secondly, potassium osmichloride was treated in the same way, but the residue weighed consisted of Os + 2KCl. From this the potassium chloride was dissolved out, recovered by evaporating the solution, and weighed separately. The volatile portion, 4HCl, was also measured by precipitation as silver chloride. In Seubert's first paper these data are given :

$K_2\text{OsCl}_6$	<i>Os.</i>	<i>2KCl.</i>	<i>4AgCl.</i>
2.5148	.....	.7796	2.9837
2.1138	.8405	.6547	2.5076

Hence, with salt proportional to 100 parts of AgCl in the last column we have—

<i>Per cent. Os.</i>	<i>Per cent. KCl.</i>	<i>AgCl : Salt.</i>
.....	31.000	84.091
39.762	30.973	84.102
		<hr/>
		Mean, 84.097, $\pm .0030$

In his second paper Seubert gives fuller data relative to the potassium osmichloride, but treats it somewhat differently. The salt was reduced by a stream of hydrogen as before, but after that the boat containing the Os + 2KCl was transferred to a platinum tube, in which, by prolonged heating in the gas, the potassium chloride was completely volatilized. The determinations of 4Cl as 4AgCl were omitted. Two series of data are given, as follows :

---

\* Ann. d. Chem., 261, 258.

$K_2OsCl_6$ .	<i>Os.</i>	<i>Per cent. Os.</i>
1.1863	.4691	39.543
.9279	.3667	39.519
1.0946	.4330	39.558
1.6055	.6351	39.558
.4495	.1778	39.555
.8646	.3417	39.521
.7024	.2781	39.593
1.2742	.5041	39.562
1.0466	.4141	39.566
		<hr/>
		Mean, 39.553, $\pm .0052$

$K_2OsCl_6$ .	$2KCl$ .	<i>Per cent. KCl.</i>
2.2032	.6820	30.955
2.0391	.6312	30.950
2.7596	.8544	30.961
2.4934	.7710	30.922
2.8606	.8843	30.913
2.8668	.5768	30.898
1.2227	.3778	30.899
		<hr/>
		Mean, 30.931
		Earlier set, $\left\{ \begin{array}{l} 31.000 \\ 30.973 \end{array} \right.$
		<hr/>

Mean of all nine determinations, 30.941,  $\pm .0079$

The single percentage of osmium in the earlier memoir is obviously to be rejected.

The ratios to examine are now as follows :

- (1.) Per cent. Os in  $Am_2OsCl_6$ , 43.459,  $\pm .0036$
- (2.)  $6AgCl : Am_2OsCl_6 : : 100 : 51.283$ ,  $\pm .0099$
- (3.)  $4AgCl : K_2OsCl_6 : : 100 : 84.097$ ,  $\pm .0030$
- (4.) Per cent. Os in  $K_2OsCl_6$ , 39.553,  $\pm .0052$
- (5.) Per cent. KCl in  $K_2OsCl_6$ , 30.951,  $\pm .0079$

To reduce these ratios we have—

Cl = 35.179, $\pm .0048$	KCl = 74.025, $\pm .0019$
K = 38.817, $\pm .0051$	AgCl = 142.287, $\pm .0037$
N = 13.935, $\pm .0021$	

Hence there are five independent values for osmium, as follows :

From (1).....	Os = 190.111, $\pm .0300$
From (2).....	" = 190.870, $\pm .0901$
From (3).....	" = 189.928, $\pm .0371$
From (4).....	" = 188.914, $\pm .0243$
From (5).....	" = 189.571, $\pm .0928$
<hr/>	
General mean.....	Os = 189.546, $\pm .0163$

If O = 16, Os = 190.990.



These figures serve to fix the place of osmium below iridium in the periodic classification of the elements, but are not concordant enough to be fully satisfactory. More determinations are evidently needed.

## IRIDIUM.

The only early determination of the atomic weight of iridium was made by Berzelius,\* who analyzed potassium iridichloride by the same method employed with the platinum and the osmium salts. The result found from a single analysis was not far from  $\text{Ir} = 196.7$ . This is now known to be too high. I have not, therefore, thought it worth while to recalculate Berzelius' figures, but give his estimation as it is stated in Roscoe and Schorlemmer's "Treatise on Chemistry."

In 1878 the matter was taken up by Seubert,† who had at his disposal 150 grammes of pure iridium. From this he prepared the iridichlorides of ammonium and potassium  $(\text{NH}_4)_2\text{IrCl}_6$  and  $\text{K}_2\text{IrCl}_6$ , which salts were made the basis of his determinations. The potassium salt was dried by gentle heating in a stream of dry chlorine.

Upon ignition of the ammonium salt in hydrogen, metallic iridium was left behind in white coherent laminae. The results obtained were as follows:

$\text{Am}_2\text{IrCl}_6$ .	<i>Ir.</i>	<i>Per cent. Ir.</i>
1.3164	.5755	43.725
1.7122	.7490	43.745
1.2657	.5536	43.739
1.3676	.5980	43.726
2.6496	1.1586	43.739
2.8576	1.2489	43.705
2.9088	1.2724	43.742

Mean, 43.732,  $\pm .0035$

The potassium salt was also analyzed by decomposition in hydrogen with special precautions. In the residue the iridium and the potassium chloride were separated after the usual method, and both were estimated. Eight analyses gave the following weights:

$\text{K}_2\text{IrCl}_6$ .	$\text{Cl}_4$ , <i>Loss.</i>	<i>Ir.</i>	<i>KCl.</i>
1.6316	.4779	.6507	.5030
2.2544	.6600	.8993	.6953
2.1290	.6238	.8488	.6560
1.8632	.5457	.7430	.5745
2.6898	.7878	1.0726	.8291
2.3719	.6952	.9459	.7308
2.6092	.7641	1.0406	.8040
2.5249	.7395	1.0070	.7775

\* Poggend. Annalen, 13, 435. 1828.

† Ber. Deutsch. Chem. Gesell., 11, 1757. 1878.

Hence we have the following percentages, reckoned on the original salt:

<i>Ir.</i>	<i>2KCl.</i>	<i>Cl<sub>4</sub>.</i>
39.881	30.829	29.290
30.890	30.842	29.277
39.868	30.813	29.300
30.876	30.835	29.289
39.877	30.825	29.287
39.879	30.811	29.310
39.882	30.814	29.285
39.883	30.792	29.288

Mean, 39.880,  $\pm .0015$     Mean, 30.820,  $\pm .0037$     Mean, 29.291,  $\pm .0024$

Joly\* studied derivatives of iridium trichloride. The salts were dried at 120°, and reduced in hydrogen. With  $\text{IrCl}_3 \cdot 3\text{KCl} \cdot 3\text{H}_2\text{O}$  he found as follows:

<i>Salt.</i>	<i>Ir.</i>	<i>KCl.</i>
1.5950	.5881	.6803
1.6386	.6037	.7000
2.6276	.9689	1.1231

These data, if the weight of the salt itself is considered, give discordant results, but the ratio  $\text{Ir} : 3\text{KCl} : : 100 : x$  is satisfactory. The values of  $x$  are as follows:

$$\begin{array}{r} 115.677 \\ 115.952 \\ 115.915 \\ \hline \end{array}$$

Mean, 115.848,  $\pm .0583$

The ammonium salt,  $\text{IrCl}_3 \cdot 3\text{NH}_4\text{Cl}$ , gave the subjoined data:

<i>Wt. of Salt.</i>	<i>Wt. of Ir.</i>	<i>Per cent. Ir.</i>
1.5772	.6627	42.017
1.6056	.6742	41.990

Mean, 42.003,  $\pm .0094$

To sum up, the ratios available for iridium are these:

- (1.) Per cent. Ir in  $\text{Am}_2\text{IrCl}_6$ , 43.732,  $\pm .0035$
- (2.) Per cent. Ir in  $\text{K}_2\text{IrCl}_6$ , 39.880,  $\pm .0015$
- (3.) Per cent. KCl in  $\text{K}_2\text{IrCl}_6$ , 30.820,  $\pm .0037$
- (4.) Per cent.  $\text{Cl}_4$  in  $\text{K}_2\text{IrCl}_6$ , 29.291,  $\pm .0024$
- (5.) Per cent. Ir in  $\text{Am}_3\text{IrCl}_6$ , 42.003,  $\pm .0094$
- (6.)  $\text{Ir} : 3\text{KCl} : : 100 : 115.848$ ,  $\pm .0583$

The data for computation are—

O = 15.879, $\pm .0003$	N = 13.935, $\pm .0021$
Cl = 35.179, $\pm .0048$	KCl = 74.025, $\pm .0019$
K = 38.817, $\pm .0051$	H = 1

And the six independent values for the atomic weight of iridium become—

From (1).....	Ir = 191.935, $\pm$ .0300
From (2). ....	" = 191.511, $\pm$ .0221
From (3).....	" = 191.604, $\pm$ .0485
From (4).....	" = 191.641, $\pm$ .0622
From (5).....	" = 191.833, $\pm$ .0641
From (6).....	" = 191.695, $\pm$ .0966
<hr/>	
General mean.....	Ir = 191.664, $\pm$ .0154

If O = 16, Ir = 193.125.

## PLATINUM.

The earliest work upon the atomic weight of this metal was done by Berzelius,\* who reduced platinous chloride and found it to contain 73.3 per cent. of platinum. Hence Pt = 193.155. In a later investigation † he studied potassium chloroplatinate,  $K_2PtCl_6$ . 6.981 parts of this salt, ignited in hydrogen, lost 2.024 of chlorine. The residue consisted of 2.822 platinum and 2.135 potassium chloride. From these data we may calculate the atomic weight of platinum in four ways:

1. From loss of Cl upon ignition..... Pt = 196.637
2. From weight of Pt in residue..... " = 195.897
3. From weight of KCl in residue..... " = 195.384
4. From ratio between KCl and Pt..... " = 195.690

The last of these values is undoubtedly the best, for it is not affected by errors due to the possible presence of moisture in the salt analyzed.

The work done by Andrews‡ is even less satisfactory than the foregoing, partly for the reason that its full details seem never to have been published. Andrews dried potassium chloroplatinate at 105°, and then decomposed it by means of zinc and water. The excess of zinc having been dissolved by treatment with acetic and nitric acids, the platinum was collected upon a filter and weighed, while the chlorine in the filtrate was estimated by Pelouze's method. Three determinations gave as follows for the atomic weight of platinum:

197.86  
197.68  
198.12

Mean, 197.887

Unfortunately, Andrews does not state how his calculations were made.

\* Poggend. Annalen, 8, 177. 1826.

† Poggend. Annalen, 13, 468. 1828.

‡ British Assoc. Report, 1852. Chem. Gazette, 10,

In 1881 Seubert\* published his determinations, basing them upon very pure chloroplatinates of potassium and ammonium. The ammonium salt,  $(\text{NH}_4)_2\text{PtCl}_6$ , was analyzed by heating in a stream of hydrogen, expelling that gas by a current of carbon dioxide, and weighing the residual metal. In three experiments the hydrochloric acid formed during such a reduction was collected in an absorption apparatus, and estimated by precipitation as silver chloride. Three series of experiments are given, representing three distinct preparations, as follows:

*Series I.*

$\text{Am}_2\text{PtCl}_6$ .	Pt.	Per cent. Pt.
2.1266	.9348	43.957
1.7880	.7858	43.948
1.8057	.7938	43.960
2.6876	1.1811	43.946
4.7674	2.0959	43.963
2.0325	.8935	43.961
		<hr/>
		Mean, 43.956, $\pm .002$

*Series II.*

$\text{Am}_2\text{PtCl}_6$ .	Pt.	Per cent. Pt.
3.0460	1.3363	43.871
2.6584	1.1663	43.876
2.3334	1.0238	43.872
1.9031	.8351	43.881
3.1476	1.3810	43.875
2.7054	1.1871	43.889
		<hr/>
		Mean, 43.876, $\pm .001$

Another portion of this preparation, recrystallized from water, of 1.4358 gm. gave 0.6311 of platinum, or 43.955 per cent.

*Series III.*

$\text{Am}_2\text{PtCl}_6$ .	Pt.	Per cent. Pt.
2.5274	1.1118	43.990
3.2758	1.4409	43.986
1.9279	.8483	44.001
2.0182	.8884	44.020
1.8873	.8303	43.994
2.2270	.9798	43.996
2.4852	1.0936	44.004
2.5362	1.1166	44.026
3.0822	1.3561	43.998
		<hr/>
		Mean, 44.001, $\pm .003$

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\* Ber. Deutsch. Chem. Gesell., 14, 865.

If these series are treated as independent and combined, giving each a weight as indicated by its probable error, and regarding the single experiment with preparation II as equal to one in the first series, we get a mean percentage of 43.907,  $\pm .0009$ . On the other hand, if we regard the twenty-two experiments as all of equal weight in one series, the mean percentage of platinum becomes 43.953,  $\pm .0078$ . Upon comparing the work with that done later by Halberstadt, the latter mean seems the fairer one to adopt.

For the chlorine estimations in the ammonium salt, Seubert gives the subjoined data. I add in the last column the weight of salt proportional to 100 parts of silver chloride.

$Am_2PtCl_6$ .	<i>Pt.</i>	$6AgCl$ .	<i>Ratio.</i>
2.7054	1.1871	5.2226	51.802
2.2748	.9958	4.3758	51.986
3.0822	1.3561	5.9496	51.805
			<hr/> Mean, 51.864, $\pm .041$

The potassium salt,  $K_2PtCl_6$ , was also analyzed by ignition in hydrogen, treatment with water, and weighing both the platinum and the potassium chloride. The weights given are as follows:

$K_2PtCl_6$ .	<i>Pt.</i>	$2KCl$ .
5.0283	2.0173	1.5440
7.0922	2.8454	2.1793
3.5475	1.4217	1.0890
3.2296	1.2941	.9904
3.5834	1.4372	1.1001
4.4232	1.7746	1.3547
4.0993	1.6444	1.2589
4.4139	1.7713	1.3516

Hence we have these percentages, reckoned on the original salt:

<i>Pt.</i>	<i>KCl.</i>
40.119	30.706
40.120	30.728
40.076	30.698
40.070	30.666
40.107	30.700
40.120	30.627
40.114	30.710
40.130	30.621
<hr/> Mean, 40.107, $\pm .005$	<hr/> Mean, 30.682, $\pm .009$

As with the ammonium salt, three experiments were made upon the potassium compound to determine the amount of chlorine (four atoms in this case) lost upon ignition in hydrogen. In the fourth column I add the amount of  $K_2PtCl_6$  corresponding to 100 parts of  $AgCl$ :

$K_2PtCl_6$	<i>Pt.</i>	$4AgCl$	<i>Ratio.</i>
6.7771	2.7158	7.9725	85.006
3.5834	1.4372	4.2270	84.774
4.4139	1.7713	5.2144	84.648
			<hr/>
			Mean, 84.809, $\pm .071$

Halberstadt,\* like Seubert, studied the chloroplatinates of potassium and ammonium, and also the corresponding double bromides and platinic bromide as well. The metal was estimated partly by reduction in hydrogen, as usual, and partly by electrolysis. Platinic bromide gave the following results :

*I. By Reduction in H.*

$PtBr_4$	<i>Pt.</i>	<i>Per cent. Pt.</i>
.6396	.2422	37.867
1.7596	.6659	37.844
.9178	.3476	37.873
1.1594	.4388	37.847
1.9608	.7420	37.842
2.0865	.7898	37.853
4.0796	1.5422	37.852
6.8673	2.5985	37.839

*II. By Electrolysis.*

1.2588	.4763	37.837
1.4937	.5649	37.819

Mean of all ten experiments, 37.847,  $\pm .0033$

The ammonium platinbromide,  $(NH_4)_2PtBr_6$ , was prepared in two ways, and five distinct lots were studied. With this salt, as well as with those which follow, the data are given in distinct series, with from one to several experiments in each group, but for present purposes it seems best to consolidate the material and so put it in more manageable form. The percentages of platinum and weights found are as follows :

*I. By Reduction in H.*

$Am_2PtBr_6$	<i>Pt.</i>	<i>Per cent. Pt.</i>
.6272	.1719	27.408
1.0438	.2865	27.447
1.1724	.3215	27.422
1.4862	.4076	27.426
1.0811	.2966	27.435
1.3383	.3672	27.437

\* Ber. Deutsch. Chem. Gesell., 17, 2962. 1884.

$Am_2PtBr_6$	<i>Pt.</i>	<i>Per cent. Pt.</i>
{ 1.0096	.2769	27.426
{ 1.1935	.3269	27.390
{ 1.3182	.3611	27.393
{ 2.2476	.6159	27.402
{ 1.3358	.3668	27.451
{ 1.7859	.4899	27.431
{ 4.1641	1.1427	27.441
{ 1.1835	.3250	27.460
{ 2.4003	.6591	27.459
{ 2.5293	.6940	27.438
{ 1.7147	.4705	27.439
{ 2.3014	.6316	27.444
{ 3.0052	.8245	27.435
{ 4.8592	1.3329	27.430
{ 1.5337	.4210	27.449
{ 2.0373	.5594	27.457
{ 2.0939	.5751	27.465

## II. By Electrolysis.

{ 1.5586	.4272	27.409
{ 1.6052	.4397	27.392
{ 3.1229	.8569	27.439
1.1612	.3180	27.386
{ 2.5817	.7081	27.427
{ 1.0231	.2809	27.456
{ 1.6744	.4591	27.418
1.6744	.4591	27.418
1.6052	.4397	27.392

Mean of all thirty-two experiments, 27.429,  $\pm .0027$

With potassium platinbromide Halberstadt found as follows:

## I. By Reduction in H.

$K_2PtBr_6$	<i>Pt.</i>	$zKBr$	<i>Per cent. Pt.</i>	<i>Per cent. KBr.</i>
{ 2.5549	.6630	.8071	25.940	31.590
{ 2.6323	.6831	.8318	25.947	31.599
{ 2.9315	.7598	.9259	25.910	31.584
{ 3.4463	.8939	1.0895	25.938	31.613
{ 4.0081	1.0404	1.2653	25.957	31.568
3.9554	1.0266	1.2495	25.954	31.589
{ 2.0794	.5388	.6558	25.911	31.538
{ 2.1735	.5635	.6849	25.926	31.511
{ 2.3099	.5986	.7297	25.914	31.590
{ 1.4085	.3645	.4446	25.880	31.565
{ 2.6166	.6772	.8279	25.881	31.640
{ 2.6729	.6923	.8469	25.900	31.684

*II. By Electrolysis.*

$K_2PtBr_6$ .	<i>Pt.</i>	$2KBr$ .	<i>Per cent. Pt.</i>	<i>Per cent. KBr.</i>
{ 2.2110	.5726	.6997	25.898	31.647
{ 3.1642	.8188	.9983	25.877	31.550
{ 1.9080	.4947	.6025	25.927	31.577
{ 1.6754	.4341	.5286	25.915	31.550
{ 1.3148	.3403	.4160	25.882	31.640
{ 1.5543	.4025	.4911	25.895	31.596

Mean of eighteen experiments, 25.915,  $\pm .0040$     31.591,  $\pm .0068$

For ammonium platinchloride Halberstadt gives the following data :

*I. By Reduction in H.*

$Am_2PtCl_6$ .	<i>Pt.</i>	<i>Per cent. Pt.</i>
{ 1.0604	.4662	43.964
{ 1.3846	.6087	43.962
{ 1.5065	.6617	43.923
{ 2.3266	1.0227	43.956
{ 1.3808	.6059	43.880
{ 1.7396	.7638	43.906
{ 2.7420	1.2068	44.011
{ 3.1882	1.4019	43.971
{ 5.4644	2.4035	43.984
3.4859	1.5321	43.951

*II. By Electrolysis.*

{ .9474	.4161	43.920
{ 1.1069	.4865	43.951
{ 1.5101	.6634	43.930
{ .5345	.2347	43.910
{ 1.6035	.7044	43.928
{ 1.9271	.8459	43.894
{ 1.1046	.4858	43.979
{ 1.4179	.6233	43.959

Mean of eighteen experiments, 43.943,  $\pm .0054$

Seubert found, 43.953,  $\pm .0078$

General mean, 43.946,  $\pm .0044$

For potassium platinchloride Halberstadt's data are—

*I. By Reduction in H.*

$K_2PtCl_6$ .	<i>Pt.</i>	$2KCl$ .	<i>Per cent. Pt.</i>	<i>Per cent. KCl</i>
{ 1.6407	.6574	.5029	40.069	30.651
{ 1.9352	.7757	.5921	40.084	30.600
{ 1.5793	.6334	.4836	40.106	30.621
{ 1.6446	.6595	.5049	40.101	30.700
{ 1.0225	.4102	.3133	40.117	30.640
{ 2.4046	.9641	.7388	40.094	30.724
{ 5.8344	2.3412	1.7905	40.127	30.688
{ 7.1732	2.8776	2.1998	40.116	30.666



*II. By Electrolysis.*

$K_2PtCl_6$ .	Pt.	$2KCl$ .	Per cent. Pt.	Per cent. $KCl$ .
{ 1.2354	.4953	.3792	40.092	30.695
{ 2.5754	1.0318	.7898	40.063	30.667
{ 1.0933	.4387	.3355	40.126	30.668
{ 1.3560	.5438	.4167	40.103	30.730
{ 1.7345	.6956	.5298	40.104	30.545
{ 2.0054	.8038	.6147	40.081	30.652
{ 2.0666	.8291	.6356	40.117	30.755
{ 1.2759	.5118	.3908	40.112	30.629
{ 1.9376	.7763	.5927	40.065	30.589
{ 2.3972	.9608	.7355	40.080	30.681
{ 2.7249	1.0929	.8364	40.108	30.691
Mean of nineteen experiments, 40.098, $\pm$ .0031				30.663, $\pm$ .0080
Seubert found, 40.107, $\pm$ .0050				30.682, $\pm$ .0090
General mean, 40.101, $\pm$ .0026				30.671, $\pm$ .0060

The work of Dittmar and M'Arthur\* on the atomic weight of platinum is difficult to discuss and essentially unsatisfactory. They investigated potassium platinchloride, and came to the conclusion that it contains traces of hydroxyl replacing chlorine and also hydrogen replacing potassium. It is also liable, they think, to carry small quantities of potassium chloride. In their determinations, which involve corrections indicated by the foregoing considerations, they are not sufficiently explicit, and give none of their actual weighings. They attempt, however, to fix the ratio  $2KCl : Pt$ , and after a number of discordant, generally high results, they give the following data for the atomic weight of platinum based upon the assumption that  $2KCl = 149.182$ :

195.54

195.48

195.60

195.37

---

Mean, 195.50,  $\pm$  .0330.

Dittmar and M'Arthur also discuss Seubert's determinations, seeking to show that the latter also, properly treated, lead to a value nearer to 195.5 than to 195. Seubert at once replied to them,† pointing out that the concordance between his determinations by very different methods (a concordance verified by Halberstadt's investigation) precluded the existence of errors due to impurities such as Dittmar and M'Arthur assumed.

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\* Trans. Roy. Soc. Edinburgh, 33, 561. 1887.

† Ber. Deutsch. Chem. Gesell., 21, 2179. 1888.

The ratios from which to compute the atomic weight of platinum are now as follows, rejecting the work of Berzelius and of Andrews:

- (1.) Percentage of Pt in ammonium platinchloride, 43.946,  $\pm .0044$
- (2.) Percentage of Pt in ammonium platinbromide, 27.429,  $\pm .0027$
- (3.) Percentage of Pt in potassium platinchloride, 40.101,  $\pm .0026$
- (4.) Percentage of Pt in potassium platinbromide, 25.915,  $\pm .0040$
- (5.) Percentage of Pt in platinic bromide, 37.847,  $\pm .0033$
- (6.) Percentage of KCl in potassium platinchloride, 30.671,  $\pm .0060$
- (7.) Percentage of KBr in potassium platinbromide, 31.591,  $\pm .0068$
- (8.)  $6\text{AgCl} : \text{Am}_2\text{PtCl}_6 :: 100 : 51.864$ ,  $\pm .041$
- (9.)  $4\text{AgCl} : \text{K}_2\text{PtCl}_6 :: 100 : 84.809$ ,  $\pm .071$
- (10.)  $2\text{KCl} : \text{Pt} :: 149.182 : 195.50$ ,  $\pm .033$

Computing with the subjoined atomic and molecular weights—

Cl = 35.179, $\pm .0048$	KCl = 74.025, $\pm .0019$
Br = 79.344, $\pm .0062$	KBr = 118.200, $\pm .0073$
K = 38.817, $\pm .0051$	AgCl = 142.287, $\pm .0037$
N = 13.935, $\pm .0021$	

we have the following ten values for platinum:

From (1) . . . . .	Pt = 193.603, $\pm .0336$
From (2) . . . . .	" = 193.493, $\pm .0248$
From (3) . . . . .	" = 193.283, $\pm .0254$
From (4) . . . . .	" = 193.684, $\pm .0344$
From (5) . . . . .	" = 193.261, $\pm .0248$
From (6) . . . . .	" = 193.938, $\pm .0746$
From (7) . . . . .	" = 194.538, $\pm .1276$
From (8) . . . . .	" = 195.836, $\pm .3515$
From (9) . . . . .	" = 193.980, $\pm .4054$
From (10) . . . . .	" = 194.017, $\pm .0331$
General mean . . . . .	Pt = 193.443, $\pm .0114$

If O = 16, Pt = 194.917.

Of these ten values the first five are obviously the most trustworthy. Their general mean is Pt = 193.414,  $\pm .0124$ ; or, if O = 16, Pt = 194.888. This result is preferable to the mean of all, even though the latter varies little from it. The five high values carry very little weight because of their larger probable errors.

## CERIUM.

Although cerium was discovered almost at the beginning of the present century, its atomic weight was not properly determined until after the discovery of lanthanum and didymium by Mosander. In 1842 the investigation was undertaken by Beringer,\* who employed several methods. His cerium salts, however, were all rose-colored, and therefore were not wholly free from didymium; and his results are further affected by a negligence on his part to fully describe his analytical processes.

First, a neutral solution of cerium chloride was prepared by dissolving the carbonate in hydrochloric acid. This gave weights of ceric oxide and silver chloride as follows. The third column shows the amount of  $CeO_2$  proportional to 100 parts of  $AgCl$ :

$CeO_2$ .	$AgCl$ .	Ratio.
.5755 grm.	1.419 grm.	40.557
.6715 "	1.6595 "	40.464
1.1300 "	2.786 "	40.560
.5366 "	1.3316 "	40.297

Mean, 40.469,  $\pm .0415$

The analysis of the dry cerium sulphate gave results as follows. In a fourth column I show the amount of  $CeO_2$  proportional to 100 parts of  $BaSO_4$ :

<i>Sulphate.</i>	$CeO_2$ .	$BaSO_4$	Ratio.
1.379 grm.	.8495 grm.	1.711 grm.	49.649
1.276 "	.7875 "	1.580 "	49.836
1.246 "	.7690 "	1.543 "	49.838
1.553 "	.9595 "	1.921 "	49.948

Mean, 49.819,  $\pm .042$

Beringer also gives a single analysis of the formate and the results of one conversion of the sulphide into oxide. The figures are, however, not valuable enough to cite.

The foregoing data involve one variation from Beringer's paper. Where I put  $CeO_2$  as found he puts  $Ce_2O_3$ . The latter is plainly inadmissible, although the atomic weights calculated from it agree curiously well with some other determinations. Obviously, the presence of didymium in the salts analyzed tends to raise the apparent atomic weight of cerium.

Shortly after Beringer, Hermann † published the results of one experiment. 23.532 grm. of anhydrous cerium sulphate gave 29.160 grm. of  $BaSO_4$ . Hence 100 parts of the sulphate correspond to 123.926 of  $BaSO_4$ .

\* Ann. Chem. Pharm., 42, 134. 1842.

† Journ. für Prakt. Chem., 30, 185. 1843.

In 1848 similar figures were published by Marignac,\* who found the following amounts of  $\text{BaSO}_4$  proportional to 100 of dry cerium sulphate :

$$\begin{array}{r} 122.68 \\ 122.00 \\ 122.51 \\ \hline \text{Mean, } 122.40, \pm .138 \end{array}$$

If we give Hermann's single result the weight of one experiment in this series, and combine, we get a mean value of 122.856,  $\pm .130$ .

Still another method was employed by Marignac. A definite mixture was made of solutions of cerium sulphate and barium chloride. To this were added, volumetrically, solutions of each salt successively, until equilibrium was attained. The figures published give maxima and minima for the  $\text{BaCl}_2$  proportional to each lot of  $\text{Ce}_2(\text{SO}_4)_3$ . In another column, using the mean value for  $\text{BaCl}_2$  in each case, I put the ratio between 100 parts of this salt and the equivalent quantity of sulphate. The latter compound was several times recrystallized :

$\text{Ce}_2(\text{SO}_4)_3$ .	$\text{BaCl}_2$ .	Ratio.
First crystallization, . . . . . 11.011 gm.	11.990 — 12.050 gm.	91.606
First crystallization, . . . . . 13.194 "	14.365 — 14.425 "	91.657
Second crystallization, . . . . 13.961 "	15.225 — 15.285 "	91.518
Second crystallization, . . . . 12.627 "	13.761 — 13.821 "	91.559
Second crystallization, . . . . 11.915 "	12.970 — 13.030 "	91.654
Third crystallization, . . . . . 14.888 "	16.223 — 16.283 "	91.602
Third crystallization, . . . . . 14.113 "	15.383 — 15.423 "	91.755
Fourth crystallization, . . . . . 13.111 "	14.270 — 14.330 "	91.685
Fourth crystallization, . . . . . 13.970 "	15.223 — 15.283 "	91.588
		Mean, 91.625, $\pm .016$

Omitting the valueless experiments of Kjerulf,† we come next to the figures published by Bunsen and Jegel‡ in 1858. From the air-dried sulphate of cerium the metal was precipitated as oxalate, which, ignited, gave  $\text{CeO}_2$ . In the filtrate from the oxalate the sulphuric acid was estimated as  $\text{BaSO}_4$  :

1.5726 gm. sulphate gave .7899 gm. $\text{CeO}_2$ and 1.6185 gm. $\text{BaSO}_4$ .
1.6967 " " .8504 " 1.7500 "

Hence, for 100 parts  $\text{BaSO}_4$ , the  $\text{CeO}_2$  is as follows :

$$\begin{array}{r} 48.804 \\ 48.575 \\ \hline \text{Mean, } 48.689, \pm .077 \end{array}$$

\* Arch. Sci. Phys. et Nat. (1), 8, 273. 1848.

† Ann. Chem. Pharm., 87, 12.

‡ Ann. Chem. Pharm., 105, 45. 1858.

One experiment was also made upon the oxalate :

.3530 grm. oxalate gave .1913  $\text{CeO}_2$  and .0506  $\text{H}_2\text{O}$ .

Hence, in the dry salt, we have 63.261 per cent. of  $\text{CeO}_2$ .

In each sample of  $\text{CeO}_2$  the excess of oxygen over  $\text{Ce}_2\text{O}_3$  was estimated by an iodometric titration ; but the data thus obtained need not be further considered.

In two papers by Rammelsberg\* data are given for the atomic weight of cerium, as follows. In the earlier paper cerium sulphate was analyzed, the cerium being thrown down by caustic potash, and the acid precipitated from the filtrate as barium sulphate :

.413 grm.  $\text{Ce}_2(\text{SO}_4)_3$  gave .244 grm.  $\text{CeO}_2$  and .513 grm.  $\text{BaSO}_4$ .

Hence  $100 \text{ BaSO}_4 = 47.563 \text{ CeO}_2$ , a value which may be combined with others, thus ; this figure being assigned a weight equal to one experiment in Bunsen's series :

Beringer .....	49.819, $\pm$ .042
Bunsen and Jegel.....	48.689, $\pm$ .077
Rammelsberg .....	47.563, $\pm$ .108
General mean.....	49.360, $\pm$ .035

It should be noted here that this mean is somewhat arbitrary, since Bunsen and Rammelsberg's cerium salts were undoubtedly freer from didymium than the material studied by Beringer.

In his later paper Rammelsberg gives these figures concerning cerium oxalate. One hundred parts gave 10.43 of carbon and 21.73 of water. Hence the dry salt should yield 48.862 per cent. of  $\text{CO}_2$ , whence  $\text{Ce} = 137.14$ .

In all of the foregoing experiments the ceric oxide was somewhat colored, the tint ranging from one shade to another of light brown according to the amount of didymium present. Still, at the best, a color remained, which was supposed to be characteristic of the oxide itself. In 1868, however, some experiments of Dr. C. Wolf† were posthumously made public, which went to show that pure ceroso-ceric oxide is white, and that all samples previously studied were contaminated with some other earth, not necessarily didymium but possibly a new substance, the removal of which tended to lower the apparent atomic weight of cerium very perceptibly.

Cerium sulphate was recrystallized at least ten times. Even after twenty recrystallizations it still showed spectroscopic traces of didymium. The water contained in each sample of the salt was cautiously estimated, and the cerium was thrown down by boiling concentrated solutions of

\* Poggend. Annalen, 55, 65 ; 108, 44.

† Amer. Journ. Science and Arts (2), 46, 53.

oxalic acid. The resulting oxalate was ignited with great care. I deduce from the weighings the percentage of  $\text{CeO}_2$  given by the *anhydrous* sulphate:

<i>Sulphate.</i>	<i>Water.</i>	<i>CeO<sub>2</sub>.</i>	<i>Per cent. CeO<sub>2</sub>.</i>
1.4542 grm.	.19419 grm.	.76305 grm.	60.559
1.4104 "	.1898 "	.7377 "	60.437
1.35027 "	.1820 "	.70665 "	60.487
			Mean, 60.494

After the foregoing experiments the sulphate was further purified by solution in nitric acid and pouring into a large quantity of boiling water. The precipitate was converted into sulphate and analyzed as before:

<i>Sulphate.</i>	<i>Water.</i>	<i>CeO<sub>2</sub>.</i>	<i>Per cent. CeO<sub>2</sub>.</i>
1.4327 grm.	.2733 grm.	.69925 grm.	60.311
1.5056 "	.2775 "	.7405 "	60.296
1.44045 "	.2710 "	.7052 "	60.300
			Mean, 60.302

From another purification the following weights were obtained:

1.4684 grm.	.1880 grm.	.7717 grm.	60.270 per cent.
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A last purification gave a still lower percentage:

1.3756 grm.	.1832 grm.	.7186 grm.	60.265 per cent.
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The last oxide was perfectly white, and was spectroscopically free from didymium. In each case the  $\text{CeO}_2$  was titrated iodometrically for its excess of oxygen. It will be noticed that in the successive series of determinations the percentage of  $\text{CeO}_2$  steadily and strikingly diminishes to an extent for which no ordinary impurity of didymium can account. The death of Dr. Wolf interrupted the investigation, the results of which were edited and published by Professor F. A. Genth.

In the light of more recent evidence, little weight can be given to these observations. All the experiments, taken equally, give a mean percentage of  $\text{CeO}_2$  from  $\text{Ce}_2(\text{SO}_4)_3$  of 60.366,  $\pm$  .0308. This mean has obviously little or no real significance.

The experiments of Wolf attracted little attention, except from Wing,\* who partially verified certain aspects of them. This chemist, incidentally to other researches, purified some cerium sulphate after the method of Wolf, and made two similar analyses of it, as follows:

<i>Sulphate.</i>	<i>Water.</i>	<i>CeO<sub>2</sub>.</i>	<i>Per cent. CeO<sub>2</sub>.</i>
1.2885 grm.	.1707 grm.	.6732 grm.	60.225
1.4090 "	.1857 "	.7372 "	60.263
			Mean, 60.244

\* Am. Journ. Sci. (2), 49, 358. 1870.

The ceric oxide in this case was perfectly white. The cerium oxalate which yielded it was precipitated boiling by a boiling concentrated solution of oxalic acid. The precipitate stood twenty-four hours before filtering.

In 1875 Buehrig's\* paper upon the atomic weight of cerium was issued. He first studied the sulphate, which, after eight crystallizations, still retained traces of free sulphuric acid. He found, furthermore, that the salt obstinately retained traces of water, which could not be wholly expelled by heat without partial decomposition of the material. These sources of error probably affect all the previously cited series of experiments, although, in the case of Wolf's work, it is doubtful whether they could have influenced the atomic weight of cerium by more than one or two tenths of a unit. Buehrig also found, as Marignac had earlier shown, that upon precipitation of cerium sulphate with barium chloride the barium sulphate invariably carried down traces of cerium. Furthermore, the ceric oxide from the filtrate always contained barium. For these reasons the sulphate was abandoned, and the atomic weight determinations of Buehrig were made with air-dried oxalate. This salt was placed in a series of platinum boats in a combustion tube behind copper oxide. It was then burned in a stream of pure, dry oxygen, and the carbonic acid and water were collected after the usual method. Ten experiments were made; in all of them the above-named products were estimated, and in five analyses the resulting ceric oxide was also weighed. By deducting the water found from the weight of the air-dried oxalate, the weight of the anhydrous oxalate is obtained, and the percentages of its constituents are easily determined. In weighing, the articles weighed were always counterpoised with similar materials. The following weights were found:

<i>Oxalate.</i>	<i>Water.</i>	<i>CO<sub>2</sub>.</i>	<i>CeO<sub>2</sub>.</i>
9.8541 gm.	2.1987 gm.	3.6942 gm.	.....
9.5368 "	2.1269 "	3.5752 "	.....
9.2956 "	2.0735 "	3.4845 "	.....
10.0495 "	2.2364 "	3.7704 "	.....
10.8249 "	2.4145 "	4.0586 "	.....
9.3679 "	2.0907 "	3.5118 "	4.6150 gm.
9.7646 "	2.1769 "	3.6616 "	4.8133 "
9.9026 "	2.2073 "	3.7139 "	4.8824 "
9.9376 "	2.2170 "	3.7251 "	4.8971 "
9.5324 "	2.1267 "	3.5735 "	4.6974 "

These figures give us the following percentages for CO<sub>2</sub> and CeO<sub>2</sub> in the anhydrous oxalate:

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\* Journ. für Prakt. Chem., 120, 222. 1875.

$CO_2$ .	$CeO_2$ .
48.256	.....
48.249	.....
48.248	.....
48.257	.....
48.257	.....
48.258	63.417
48.257	63.436
48.262	63.446
48.249	63.429
48.253	63.430
Mean, 48.2546 $\pm$ .001	Mean, 63.4316, $\pm$ .0032

These results could not be appreciably affected by combination with the single oxalate experiments of Jegel and of Rammelsberg, and the latter may therefore be ignored.

Robinson's work, published in 1884,\* was based upon pure cerium chloride, prepared by heating dry cerium oxalate in a stream of dry, gaseous hydrochloric acid. This compound was titrated with standard solutions of pure silver, prepared according to Stas, and these were weighed, not measured. In the third column I give the ratio between  $CeCl_3$  and 100 parts of silver :

$CeCl_3$ .	<i>Ag.</i>	<i>Ratio.</i>
5.5361	7.26630	76.189
6.0791	7.98577	76.172
6.4761	8.50626	76.133
6.98825	9.18029	76.122
6.6873	8.78015	76.164
7.0077	9.20156	76.158
6.9600	9.13930	76.150
	Mean, 76.155, $\pm$ .0065	

Reduced to a vacuum this becomes 76.167.

In a later paper,† Robinson discusses the color of ceric oxide, and criticises the work of Wolf. He shows that the pure oxide is not white, and makes it appear probable that Wolf's materials were contaminated with compounds of lanthanum. He also urges that Wolf's cerium sulphate could not have been absolutely definite, because of defects in the method by which it was dehydrated.

Brauner,‡ in 1885, investigated cerium sulphate with extreme care, and appears to have obtained material free from all other earths and absolutely homogeneous. The anhydrous salt was calcined with all

\* Chemical News, 50, 251. Nov. 28, 1884. Proc. Roy. Soc., 37, 150.

† Chemical News, 54, 229. 1886.

‡ Sitzungs. Wien. Akad., Bd. 92. July, 1885.



necessary precautions, and the data obtained, reduced to a vacuum, were as follows :

$Ce_2(SO_4)_3$ .	$CeO_2$ .	<i>Per cent. <math>CeO_2</math>.</i>
2.16769	1.31296	60.5693
2.43030	1.47205	60.5707
2.07820	1.25860	60.5620
2.21206	1.33989	60.5721
1.28448	.77845	60.6043
1.95540	1.18436	60.5687
2.46486	1.49290	60.5673
2.04181	1.23733	60.5997
2.17714	1.31878	60.5739
2.09138	1.26654	60.5605
2.21401	1.34139	60.5863
2.44947	1.48367	60.5711
2.22977	1.35073	60.5771
2.73662	1.65699	60.5486
2.62614	1.59050	60.5642
1.67544	1.01470	60.5632
1.57655	.95540	60.6007
2.72882	1.65256	60.5600
2.10455	1.27476	60.5716
2.10735	1.27698	60.5965
2.43557	1.47517	60.5692
3.01369	1.82524	60.5649
4.97694	3.01372	60.5537

Mean, 60.5729,  $\pm .0021$

This mean completely outweighs the work done by Wolf and Wing, so that upon combination the latter practically vanish. Wing's mean is arbitrarily given equal weight with Wolf's, and the combination is as follows:

Wolf.....	60.566, $\pm .0308$
Wing.....	60.244, $\pm .0308$
Brauner.....	60.5729, $\pm .0021$
General mean.....	60.566, $\pm .0021$

In 1895 several papers upon the cerite earths were published by Schutzenger.\* In the first of these a single determination of atomic weight is given. Pure  $CeO_2$ , of a yellowish white color, was converted into sulphate, which was dried in a current of dry air at  $440^\circ$ . This salt, dissolved in water, was poured into a hot solution of caustic soda, made from sodium, and, after filtration and washing, the filtrate, acidulated with hydrochloric acid, was precipitated with barium chloride. The trace of sulphuric acid retained by the cerium hydroxide was recovered by re-solution and a second precipitation, and added to the main amount.

\* Compt. Rend., 120, pp. 663, 962, and 1143. 1895.

100 parts of  $\text{Ce}_2(\text{SO}_4)_3$  gave 123.30 of  $\text{BaSO}_4$ . This may be assigned equal weight with one experiment in Marignac's series, giving the following combination :

Hermann.....	123.926, $\pm .238$
Marignac.....	122.40, $\pm .138$
Schutzenberger.....	123.30, $\pm .238$
General mean.....	122.958, $\pm .1139$

Schutzenberger, criticising Brauner's work, claims that the latter was affected by a loss of oxygen during the calcination of the cerium dioxide.

In his second and third papers Schutzenberger describes the results obtained upon the fractional crystallization of cerium sulphate. Preparations were thus made yielding oxides of various colors—canary yellow, rose, yellowish rose, reddish, and brownish red. These oxides, by synthesis of sulphates, the barium-sulphate method, etc., gave varying values for the atomic weight of cerium, ranging from 135.7 to 143.3. Schutzenberger therefore infers that cerium oxide from cerite contains small quantities of another earth of lower molecular weight; but the results as given are not sufficiently detailed to be conclusive. The third paper is essentially a continuation of the second, with reference to the didymiums.

Schutzenberger's papers were promptly followed by one from Brauner,\* who claims priority in the matter of fractionation, and gives some new data, the latter tending to show that cerium oxide is a mixture of at least two earths. One of these, of a dark salmon color, he ascribes to a new element, "meta-cerium." The other he calls cerium, and gives for it a preliminary atomic weight determination. The pure oxalate, by Gibbs' method, gave 46.934 per cent. of  $\text{CeO}_2$ , and, on titration with potassium permanganate, 29.503 and 29.506 per cent. of  $\text{C}_2\text{O}_3$ . Hence  $\text{Ce} = 138.799$ . In mean, this ratio may be written—

$$3\text{C}_2\text{O}_3 : 2\text{CeO}_2 :: 29.5045 : 46.934,$$

and to each of its numerical terms we may roughly assign the probable error  $\pm .001$ . This is derived from the average of the two titrations, and is altogether arbitrary.

The ratios, good and bad, for cerium now are—

- (1.)  $\text{Ce}_2(\text{SO}_4)_3 : 3\text{BaSO}_4 :: 100 : 122.958, \pm .1139$
- (2.)  $3\text{BaSO}_4 : 2\text{CeO}_2 :: 100 : 49.360, \pm .035$
- (3.)  $3\text{BaCl}_2 : \text{Ce}_2(\text{SO}_4)_3 :: 100 : 91.625, \pm .016$
- (4.)  $3\text{AgCl} : \text{CeO}_2 :: 100 : 40.469, \pm .0415$
- (5.) Percentage  $\text{CeO}_2$  from  $\text{Ce}_2(\text{SO}_4)_3$ , 60.566,  $\pm .0021$
- (6.) Percentage  $\text{CeO}_2$  from  $\text{Ce}_2(\text{C}_2\text{O}_4)_3$ , 63.4316,  $\pm .0032$
- (7.) Percentage  $\text{CO}_2$  from  $\text{Ce}_2(\text{C}_2\text{O}_4)_3$ , 48.2546,  $\pm .001$ .
- (8.)  $3\text{Ag} : \text{CeCl}_3 :: 100 : 76.167, \pm .0065$
- (9.)  $3\text{C}_2\text{O}_3 : 2\text{CeO}_2 :: 29.5045, \pm .001 : 46.934, \pm .001$

\*Chem. News, 71, 283.

To reduce these ratios we have—

O	= 15.879, $\pm$ .0003	C	= 11.920, $\pm$ .0004
Cl	= 35.179, $\pm$ .0048	S	= 31.828, $\pm$ .0015
Ag	= 107.108, $\pm$ .0031	Ba	= 136.392, $\pm$ .0086
AgCl	= 142.287, $\pm$ .0037		

From the ratios, with these intermediate data, we can get two values for the molecular weight of  $\text{Ce}_2(\text{SO}_4)_3$ , and five for that of  $\text{CeO}_2$ . For cerium sulphate we have—

From (1).....	$\text{Ce}_2(\text{SO}_4)_3$	= 565.404, $\pm$ .1670
From (3).....	“	= 568.304, $\pm$ .1054
General mean.....		$\text{Ce}_2(\text{SO}_4)_3$ = 567.478, $\pm$ .0891

Hence  $\text{Ce} = 140.723$ ,  $\pm$  .0451.

For ceric oxide the values are—

From (2).....	$\text{CeO}_2$	= 171.577, $\pm$ .1218
From (4).....	“	= 172.746, $\pm$ .1772
From (5).....	“	= 170.879, $\pm$ .0115
From (6).....	“	= 172.125, $\pm$ .0177
From (9).....	“	= 170.557, $\pm$ .0076
General mean.....		$\text{CeO}_2$ = 170.827, $\pm$ .0060

And  $\text{Ce} = 139.069$ ,  $\pm$  .0061.

For cerium itself, four independent values are now calculable, as follows:

From molecular weight of sulphate...	$\text{Ce}$	= 140.723, $\pm$ .0451
From molecular weight of dioxide...	“	= 139.069, $\pm$ .0061
From ratio (8).....	“	= 139.206, $\pm$ .0263
From ratio (7).....	“	= 140.516, $\pm$ .0047
General mean.....		$\text{Ce} = 140.113$ , $\pm$ .0036

If  $\text{O} = 16$ ,  $\text{Ce} = 141.181$ .

It must be admitted that this combination is of very questionable utility. Its component means vary too widely from each other, and involve too many uncertainties. Furthermore, Schutzenberger and Brauner both impugn the homogeneity of the supposed element, as it has hitherto been recognized. Even if no “meta-elements” are involved in the discussion, it seems clear, on chemical grounds, that the two lower values are really preferable to the two higher, and that ratio (7) receives excessive weight. The general mean obtained is probably a full unit too high. The value 139.1 is perhaps nearly correct.

## LANTHANUM.

Leaving out of account the work of Mosander, and the valueless experiments of Choubine, we may consider the estimates of the atomic weight of lanthanum which are due to Hermann, Rammelsberg, Marignac, Czudnowicz, Holzmann, Zschiesche, Erk, Cleve, Brauner, Bauer, and Bettendorff.

From Rammelsberg\* we have but one analysis. .700 grm. of lanthanum sulphate gave .883 grm. of barium sulphate. Hence 100 parts of  $\text{BaSO}_4$  are equivalent to 79.276 of  $\text{La}_2(\text{SO}_4)_3$ .

Marignac,† working also with the sulphate of lanthanum, employed two methods. First, the salt in solution was mixed with a slight excess of barium chloride. The resulting barium sulphate was filtered off and weighed; but, as it contained some occluded lanthanum compounds, its weight was too high. In the filtrate the excess of barium was estimated, also as sulphate. This last weight of sulphate, deducted from the total sulphate which the whole amount of barium chloride could form, gave the sulphate actually proportional to the lanthanum compound. The following weights are given:

$\text{La}_2(\text{SO}_4)_3$ .	$\text{BaCl}_2$ .	1st $\text{BaSO}_4$ .	2d $\text{BaSO}_4$ .
4.346 grm.	4.758 grm.	5.364 grm.	.115 grm.
4.733 "	5.178 "	5.848 "	.147 "

Hence we have the following quantities of  $\text{La}_2(\text{SO}_4)_3$  proportional to 100 parts of  $\text{BaSO}_4$ . Column A is deduced from the first  $\text{BaSO}_4$  and column B from the second, after the manner above described:

A.	B.
81.022	83.281
80.934	83.662
Mean, 80.978, $\pm$ .030	Mean, 83.471, $\pm$ .128
From A.....	La = 138.47
From B.....	" = 147.13

A agrees best with other determinations, although, theoretically, it is not so good as B.

Marignac's second method, described in the same paper with the foregoing experiments, consisted in mixing solutions of  $\text{La}_2(\text{SO}_4)_3$  with solutions of  $\text{BaCl}_2$ , titrating one with the other until equilibrium was established. The method has already been described under cerium. The weighings

\* Poggend. Annalen, 55, 65.

† Arch. Sci. Phys. et Nat. (1), 11, 29. 1849.

give maxima and minima for  $\text{BaCl}_2$ . In another column I give  $\text{La}_2(\text{SO}_4)_3$  proportional to 100 parts of  $\text{BaCl}_2$ , mean weights being taken for the latter:

$\text{La}_2(\text{SO}_4)_3$ .	$\text{BaCl}_2$ .	Ratio.
11.644 gm.	12.765 — 12.825 gm.	91.004
12.035 "	13.195 — 13.265 "	90.968
10.690 "	11.669 — 11.749 "	91.297
12.750 "	13.920 — 14.000 "	91.332
10.757 "	11.734 — 11.814 "	91.362
12.672 "	13.813 — 13.893 "	91.475
9.246 "	10.080 — 10.160 "	91.364
10.292 "	11.204 — 11.264 "	91.615
10.192 "	11.111 — 11.171 "	91.482

Mean, 91.322,  $\pm .048$

Hence  $\text{La} = 140.2$ .

Although not next in chronological order, some still more recent work of Marignac's\* may properly be considered here. The salt studied was the sulphate of lanthanum, purified by repeated crystallizations. In two experiments the salt was calcined, and the residual oxide weighed; in two others the lanthanum was precipitated as oxalate, and converted into oxide by ignition. The following percentages are given for  $\text{La}_2\text{O}_3$ :

57.56	} By calcination.
57.58	
57.50	} Ppt. as oxalate.
57.55	

Mean, 57.5475,  $\pm .0115$

The atomic weight determinations of Holzmänn† were made by analyses of the sulphate and iodate of lanthanum, and the double nitrate of magnesium and lanthanum. In the sulphate experiments the lanthanum was first thrown down as oxalate, which, on ignition, yielded oxide. The sulphuric acid was precipitated as  $\text{BaSO}_4$  in the filtrate.

$\text{La}_2(\text{SO}_4)_3$ .	$\text{La}_2\text{O}_3$ .	$\text{BaSO}_4$ .
.9663 gm.	.5157 gm.	1.1093 gm.
.6226 "	.3323 "	.7123 "
.8669 "	.4626 "	.9869 "

These results are best used by taking the ratio between the  $\text{BaSO}_4$ , put at 100, and the  $\text{La}_2\text{O}_3$ . The figures are then as follows:

46.489
46.652
46.873

Mean, 46.671,  $\pm .075$

\* Ann. Chim. Phys. (4), 30, 68. 1873.

† Journ. für Prakt. Chem., 75, 321. 1858.

In the analyses of the iodate the lanthanum was thrown down as oxalate, as before. The iodic acid was also estimated volumetrically, but the figures are hardly available for present discussion. The following percentages of  $\text{La}_2\text{O}_3$  were found :

23.454  
23.419  
23.468

Mean, 23.447,  $\pm .0216$

The formula of this salt is  $\text{La}_2(\text{IO}_3)_6 \cdot 3\text{H}_2\text{O}$ .

The double nitrate,  $\text{La}_2(\text{NO}_3)_6 \cdot 3\text{Mg}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ , gave the following analytical data :

<i>Salt.</i>	<i>H<sub>2</sub>O.</i>	<i>MgO.</i>	<i>La<sub>2</sub>O<sub>3</sub>.</i>
.5327 grm.	.1569 grm.	.0417 grm.	.1131 grm.
.5931 "	.1734 "	.0467 "	.1262 "
.5662 "	.1647 "	.0442 "	.1197 "
.3757 "	.....	.0297 "	.0813 "
.3263 "	.....	.0256 "	.0693 "

These weighings give the subjoined percentages of  $\text{La}_2\text{O}_3$  :

21.231  
21.278  
21.141  
21.640  
21.238

Mean, 21.3056,  $\pm .058$

These data of Holzmann give values for the molecular weight of  $\text{La}_2\text{O}_3$  as follows :

From sulphate .....	$\text{La}_2\text{O}_3 = 322.460$
From iodate.....	" = 320.726
From magnesian nitrate.....	" = 322.904

Czudnowicz\* based his determination of the atomic weight of lanthanum upon one analysis of the air-dried sulphate. The salt contained 22.741 per cent. of water.

.598 grm. gave .272 grm.  $\text{La}_2\text{O}_3$  and .586 grm.  $\text{BaSO}_4$ .

The  $\text{La}_2\text{O}_3$  was found by precipitation as oxalate and ignition. The  $\text{BaSO}_4$  was thrown down from the filtrate. Reduced to the standards already adopted, these data give for the percentage of  $\text{La}_2\text{O}_3$  in the anhydrous sulphate the figure 58.668. 79.117 parts of the salt are proportional to 100 parts of  $\text{BaSO}_4$ .

\* Journ. für Prakt. Chem., So. 33. 1860.

Hermann\* studied both the sulphate and the carbonate of lanthanum. From the anhydrous sulphate, by precipitation as oxalate and ignition, the following percentages of  $\text{La}_2\text{O}_3$  were obtained :

57.690  
57.663  
57.610

Mean, 57.654,  $\pm .016$

The carbonate, dried at  $100^\circ$ , gave the following percentages :

68.47  $\text{La}_2\text{O}_3$ .  
27.67  $\text{CO}_2$ .  
3.86  $\text{H}_2\text{O}$ .

Reckoning from the ratio between  $\text{CO}_2$  and  $\text{La}_2\text{O}_3$ , the molecular weight of the latter becomes 324.254.

Zschiesche's† experiments consist of six analyses of lanthanum sulphate, which salt was dehydrated at  $230^\circ$ , and afterwards calcined. I subjoin his percentages, and in a fourth column deduce from them the percentage of  $\text{La}_2\text{O}_3$  in the *anhydrous* salt :

$\text{H}_2\text{O}$ .	$\text{SO}_3$ .	$\text{La}_2\text{O}_3$ .	$\text{La}_2\text{O}_3$ in Anhydrous Salt.
22.629	33.470	43.909	56.745
22.562	33.306	44.132	56.964
22.730	33.200	44.070	57.034
22.570	33.333	44.090	56.947
22.610	33.160	44.240	57.150
22.630	33.051	44.310	57.277

Mean, 57.021,  $\pm .051$

Erk‡ found that .474 grm. of  $\text{La}_2(\text{SO}_4)_3$ , by precipitation as oxalate and ignition, gave .2705 grm. of  $\text{La}_2\text{O}_3$ , or 57.068 per cent. .7045 grm. of the sulphate also gave .8815 grm. of  $\text{BaSO}_4$ . Hence 100 parts of  $\text{BaSO}_4$  are equivalent to 79.921 of  $\text{La}_2(\text{SO}_4)_3$ .

From Cleve we have two separate investigations relative to the atomic weight of lanthanum. In his first series§ strongly calcined  $\text{La}_2\text{O}_3$ , spectroscopically pure, was dissolved in nitric acid, and then, by evaporation with sulphuric acid, converted into sulphate :

1.9215 grm. $\text{La}_2\text{O}_3$ gave	3.3365 grm. sulphate.	57.590 per cent.
2.0570        "        "	3.5705        "        "	57.611        "        "
1.6980        "        "	2.9445        "        "	57.667        "        "
2.0840        "        "	3.6170        "        "	57.617        "        "
1.9565        "        "	3.3960        "        "	57.612        "        "

Mean, 57.619,  $\pm .0085$

\* Journ. für Prakt. Chem., 82, 396. 1861.

† Journ. für Prakt. Chem., 104, 174.

‡ Jenaisches Zeitschrift, 6, 306. 1871.

§ K. Svensk. Vet. Akad. Handlingar, Bd. 2, No. 7. 1874.

From the last column, which indicates the percentage of  $\text{La}_2\text{O}_3$  in  $\text{La}_2(\text{SO}_4)_3$ , we get, if  $\text{SO}_3 = 80$ ,  $\text{La} = 139.15$ .

In his second paper,\* published nine years later, Cleve gives results similarly obtained, but with lanthanum oxide much more completely freed from other earths. The data are as follows, lettered to correspond to different fractions of the material studied :

B.	.8390	gram.	$\text{La}_2\text{O}_3$	gave	1.4600	sulphate.	57.466	per cent.
C.	{	1.1861	"		2.0643	"	57.458	"
		.8993	"		1.5645	"	57.482	"
		.8685	"		1.5108	"	57.486	"
		.8515	"		1.4817	"	57.468	"
D.	{	.6486	"		1.1282	"	57.490	"
		.7329	"		1.2746	"	57.500	"
E.		1.2477	"		2.1703	"	57.490	"
F.	{	1.1621	"		2.0217	"	57.481	"
		1.5749	"		2.7407	"	57.463	"
G.	{	1.3367	"		2.3248	"	57.497	"
		1.4455	"		2.5146	"	57.484	"

Mean, 57.480,  $\pm .0040$

Hence with  $\text{SO}_3 = 80$ ,  $\text{La} = 138.22$ .

From Brauner we also have two sets of determinations, both based upon the conversion of pure  $\text{La}_2\text{O}_3$  into  $\text{La}_2(\text{SO}_4)_3$ .

In his first paper, Brauner † gives only two syntheses, as follows :

1.75933	gram.	$\text{La}_2\text{O}_3$	gave	3.05707	$\text{La}_2(\text{SO}_4)_3$ .	57.566	per cent.
.92417	"			1.60589	"	57.549	"

Mean, 57.5575

This mean we may regard as of equal weight with Marignac's, and assign to it the same probable error.

In Brauner's second paper ‡ six experiments are given ; but the weights are affected by a misprint in the second determination, which I am unable to correct. Only five of the syntheses, therefore, are given below.

.7850	gram.	$\text{La}_2\text{O}_3$	gave	1.3658	$\text{La}_2(\text{SO}_4)_3$ .	57.476	per cent.
2.1052	"			3.6633	"	57.467	"
1.0010	"			1.7411	"	57.525	"
1.3807	"			2.4021	"	57.479	"
1.5275	"			2.6588	"	57.451	"

Mean, 57.480,  $\pm .0084$

Brauner's weighings are all reduced to a vacuum.

Both Bauer and Bettendorff made their determinations of the atomic

\* K. Svensk. Vet. Akad. Handlingar, No. 2, 1883.

† Journ. Chem. Soc., Feb., 1882, p. 68.

‡ Sitzungsab. Wien. Akad., June, 1882, Bd. 86, II Abth.



weight of lanthanum by the same general method as the preceding Bauer's data\* are as follows:

.6431	gram.	$\text{La}_2\text{O}_3$	gave	1.1171	sulphate.	57.569	per cent.
.7825		"		1.3613	"	57.482	"
1.0112		"		1.7571	"	57.549	"
.7325		"		1.2725	"	57.564	"

Mean, 57.541,  $\pm .0136$

Bettendorff found †—

.9146	gram.	$\text{La}_2\text{O}_3$	gave	1.5900	sulphate.	57.522	per cent.
.9395		"		1.6332	"	57.525	"
.9133		"		1.5877	"	57.523	"
1.0651		"		1.8515	"	57.526	"

Mean, 57.524,  $\pm .0006$

We may now combine the similar means into general means, and deduce a value for the atomic weight of lanthanum. For the percentage of oxide in sulphate we have estimates as follows. The single experiments of Czudnowicz and of Erk are assigned the probable error and weight of a single experiment in Hermann's series:

Czudnowicz.. . . . .	58.668, $\pm .027$
Erk.....	57.068, $\pm .027$
Hermann .....	57.654, $\pm .016$
Zschiesche. ....	57.021, $\pm .051$
Marignac.....	57.5475, $\pm .0115$
Cleve, earlier series.....	57.619, $\pm .0085$
Cleve, later series.....	57.480, $\pm .0040$
Brauner, earlier series.....	57.5575, $\pm .0115$
Brauner, later series.....	57.480, $\pm .0084$
Bauer.....	57.541, $\pm .0136$
Bettendorff.....	57.524, $\pm .0006$

General mean..... 57.522,  $\pm .00059$

This result is practically identical with that of Bettendorff, whose work seems to receive excessive weight. The figure, however, cannot be far out of the way.

For the quantity of  $\text{La}_2(\text{SO}_4)_3$  proportional to 100 parts of  $\text{BaSO}_4$ , we have five experiments, which may be given equal weight and averaged together:

Marignac....	81.022
Marignac .....	80.934
Rammelsberg.....	79.276
Czudnowicz.....	79.117
Erk.....	79.921

Mean, 80.054,  $\pm .270$

\* Freiburg Inaugural Dissertation, 1884.

† Ann. d. Chem., 256, 168.

In all, there are six ratios from which to calculate :

- (1.) Percentage of  $\text{La}_2\text{O}_3$  in  $\text{La}_2(\text{SO}_4)_3$ , 57.522,  $\pm .00059$
- (2.)  $3\text{BaCl}_2 : \text{La}_2(\text{SO}_4)_3 :: 100 : 91.322$ ,  $\pm .048$ —Marignac
- (3.)  $3\text{BaSO}_4 : \text{La}_2(\text{SO}_4)_3 :: 100 : 80.054$ ,  $\pm .270$
- (4.)  $3\text{BaSO}_4 : \text{La}_2\text{O}_3 :: 100 : 46.671$ ,  $\pm .075$ —Holzmann
- (5.) Percentage of  $\text{La}_2\text{O}_3$  in iodate, 23.447,  $\pm .0216$ —Holzmann
- (6.) Percentage of  $\text{La}_2\text{O}_3$  in magnesian nitrate, 21.3056,  $\pm .058$ —Holzmann

Hermann's single experiment on the carbonate is omitted from this scheme as being unimportant.

For the reduction of these data we have—

O = 15.879, $\pm .0003$	N = 13.935, $\pm .0021$
Cl = 35.179, $\pm .0048$	C = 11.920, $\pm .0004$
I = 125.888, $\pm .0069$	Mg = 24.100, $\pm .0011$
S = 31.828, $\pm .0015$	Ba = 136.392, $\pm .0086$

For lanthanum sulphate two values are obtainable :

From (2) . . . . .	$\text{La}_2(\text{SO}_4)_3 = 566.425$ , $\pm .2999$
From (3) . . . . .	" = 556.542, $\pm 1.8729$
General mean . . . . .	$\text{La}_2(\text{SO}_4)_3 = 566.182$ , $\pm .2961$

Hence  $\text{La} = 140.075$ ,  $\pm .1481$ .

For the oxide there are four independent values, as follows :

From (1) . . . . .	$\text{La}_2\text{O}_3 = 322.825$ , $\pm .0090$
From (4) . . . . .	" = 322.460, $\pm .5215$
From (5) . . . . .	" = 320.726, $\pm .3159$
From (6) . . . . .	" = 322.924, $\pm .9107$

A glance at these figures shows that the first alone deserves consideration, and that a combination of all would vary inappreciably from it. Taking, then,  $\text{La}_2\text{O}_3 = 322.825$ ,  $\pm .0090$ , we get—

$$\text{La} = 137.594, \pm .0046;$$

or, with  $\text{O} = 16$ ,  $\text{La} = 138.642$ .

If we take the concordant results of Cleve's and Brauner's later series, which give the percentage of  $\text{La}_2\text{O}_3$  in  $\text{La}_2(\text{SO}_4)_3$  as 57.480, then  $\text{La} = 137.316$ . Possibly this value may be better than the other, but the evidence is not conclusive.

## THE DIDYMIUMS.

Leaving Mosander's early experiments out of account, the atomic weight of the so-called "didymium" was determined by Marignac, Hermann, Zschiesche, Erk, Cleve, Brauner, and Bauer. All of these data now have only historical value, and may be disposed of very briefly.

Marignac\* determined the ratios between didymium sulphate and barium sulphate, between silver chloride and didymia, and between didymium sulphate and didymium oxide. The other determinations all relate to the sulphate-oxide ratio. Leaving all else out of account, the earlier data for the percentage of  $\text{Di}_2\text{O}_3$  in  $\text{Di}_2(\text{SO}_4)_3$  are as follows. The atomic weight of Di in the last column is based upon  $\text{SO}_3 = 80$ :

	<i>Per cent. <math>\text{Di}_2\text{O}_3</math>.</i>	<i>At. Wt. Di.</i>
Marignac, † five experiments . . . . .	58.270	143.56
Hermann, ‡ one experiment . . . . .	58.140	142.67
Zschiesche, § five experiments . . . . .	57.926	141.21
Erk,    two experiments . . . . .	58.090	142.33
Cleve, ¶ six experiments . . . . .	58.766	147.02
Brauner, ** three experiments . . . . .	58.681	146.42

The discordance of the determinations is manifest, and yet up to 1883 the elementary nature of didymium seems to have been undoubted. In that year, however, Cleve and Brauner both showed, independently, that the didymia previously studied by them contained samaria, and that source of disturbance was eliminated.

In Brauner's investigation †† the didymium compounds were carefully fractionated, and the determinations of atomic weight were made by synthesis of the sulphate from the oxide in the usual way. Neglecting details, his first series gave results as follows:

<i>Per cent. <math>\text{Di}_2\text{O}_3</math>.</i>	<i>At. Wt.</i>
58.506	145.36
58.526	145.50
58.500	145.31
58.515	145.42
58.531	145.53

\* Two papers: Arch. Sci. Phys. et Nat. (1), 11, 29. 1849. Ann. Chim. Phys. (3), 38, 148. 1853.

† Ann. Chim. Phys. (3), 38, 148. 1853.

‡ Journ. für Prakt. Chem., 82, 367. 1861.

§ Journ. für Prakt. Chem., 107, 74.

|| Jenaisches Zeitschrift, 6, 306. 1871.

¶ K. Svensk. Vet. Akad. Handl., Bd. 2, No. 8. 1874.

\*\* Berichte, 15, 109. 1882.

†† Journ. Chem. Soc., June, 1883. The values given are as computed by Brauner, with O = 16 and S = 32.07.

Another determination, with material refractionated from that used in his investigation of the previous year, gave 58.512 per cent.  $\text{Di}_2\text{O}_3$  and  $\text{Di} = 145.40$ .

These determinations, although concordant among themselves, are still about a unit lower than those published in 1882, indicating that in the earlier research some earth of higher molecular weight was present. Accordingly, another series of fractionations was carried out, and the several fractions of "didymia" obtained gave the following values:

<i>Fraction.</i>	<i>Per cent. <math>\text{Di}_2\text{O}_3</math>.</i>	<i>At. Wt. "Di."</i>
1.....	58.355	144.32
2.....	58.479	145.16
3.....	58.510	145.39
4.....	58.755	147.10
5.....	{ 59.071	149.35
	{ 59.086	149.46

The last fraction is evidently near samaria ( $\text{Sm} = 150$ ), and this earth was proved to be present by a study of the absorption spectra of the material investigated.

Similar results, but in some respects more explicit, were obtained by Cleve,\* who also found that his earlier research had been vitiated by the presence of samaria. He gives two series of syntheses of sulphate from oxide, with two different lots of material, after eliminating samaria, and obtains, computing with  $\text{SO}_3 = 80$ , values for  $\text{Di}$  as follows:

*First Series.*

<i>Per cent. <math>\text{Di}_2\text{O}_3</math>.</i>	<i>At. Wt. Di.</i>
58.088	142.31
58.113	142.49
58.047	142.03
58.099	142.39
58.104	142.42
58.098	142.38
58.104	142.42
58.103	142.42
58.070	142.19
58.079	142.25

*Second Series.*

<i>Per cent. <math>\text{Di}_2\text{O}_3</math>.</i>	<i>At. Wt. Di.</i>
58.125	142.57
58.093	142.35
58.088	142.31
58.111	142.47
58.056	142.10
58.097	142.38
58.057	142.10

In short, the atomic weight of this "didymium" is not far from 142.

\* Bull. Soc. Chim., 39, 289. 1883. Öfv. K. Vet. Akad. Förhandl., No. 2, 1883.

Bauer's little known determinations\* were also made by the synthesis of the sulphate. They have corroborative value and are as follows :

<i>Per cent. <math>Di_2O_3</math>.</i>	<i>At. Wt. Di.</i>
58.285	143.56
58.100	142.40
58.133	142.64
58.098	142.38

In 1885 all of the foregoing determinations were practically brushed aside by Auer von Welsbach,† who by the most laborious fractionations proved that the so-called “didymia” was really a mixture of oxides, whose metals he names neodidymium and praseodidymium, names which are now commonly shortened into neodymium and praseodymium. One of these metals gives deep rose-colored salts, the other forms green compounds, and the difference of color is almost as strongly marked as in the cases of cobalt and nickel. Their atomic weights, determined by the sulphate method, are given by Welsbach as —

$$\text{Pr} = 143.6$$

$$\text{Nd} = 140.8$$

No further details as to these determinations are cited, and whether they rest upon  $O = 16$ ,  $SO_3 = 80$ , or  $O = 15.96$  is uncertain. Fuller determinations are evidently needed.

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\* Freiburg Inaugural Dissertation, 1884.

† Monatsh. Chem., 6, 490. 1885.

## SCANDIUM.

Cleve,\* who was the first to make accurate experiments on the atomic weight of this metal, obtained the following data: 1.451 grm. of sulphate, ignited, gave .5293 grm. of  $\text{Sc}_2\text{O}_3$ . .4479 grm. of  $\text{Sc}_2\text{O}_3$ , converted into sulphate, yielded 1.2255 grm. of the latter, which, upon ignition, gave .4479 grm. of  $\text{Sc}_2\text{O}_3$ . Hence, for the percentage of  $\text{Sc}_2\text{O}_3$  in  $\text{Sc}_2(\text{SO}_4)_3$  we have:

$$\begin{array}{r} 36.478 \\ 36.556 \\ \hline 36.556 \\ \text{Mean, } 36.530, \pm .0175 \end{array}$$

Hence, if  $\text{SO}_3 = 79.465$ ,  $\text{Sc} = 44.882$ .

Later results are those of Nilson,† who converted scandium oxide into the sulphate. I give in a third column the percentage of oxide in sulphate:

.3379 grm. $\text{Sc}_2\text{O}_3$ gave .9343 grm. $\text{Sc}_2(\text{SO}_4)_3$ .	36.166 per cent.
.3015           "           .8330           "	36.194   "
.2998           "           .8257           "	36.187   "
.3192           "           .8823           "	36.178   "
	<hr/>
	Mean, 36.181, $\pm .004$

Hence  $\text{Sc} = 43.758$ .

Combining the two series, we have—

Cleve.....	36.530, $\pm .0175$
Nilson .....	36.181, $\pm .0040$
	<hr/>
General mean.....	36.190, $\pm .0039$

Hence, with  $\text{SO}_3 = 79.465, \pm .00175$ ,

$$\text{Sc} = 43.784, \pm .0085.$$

If  $\text{O} = 16$ ,  $\text{Sc} = 44.118$ .

As between the two values found, the presumption is in favor of the lower. The most obvious source of error would be the presence in the scandia of earths of higher molecular weight.

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\* Compt. Rend., 89, 419.

† Compt. Rend., 91, 118.

## YTTRIUM.

All the regular determinations of the atomic weight of yttrium depend upon analyses or syntheses of the sulphate. A series of analyses of the oxalate, however, by Berlin,\* is sometimes cited, and the data are as follows. In three experiments upon the salt  $\text{Yt}_2(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$  the subjoined percentages of oxide were found:

45.70
45.65
45.72
Mean, 45.69, $\pm .0141$

Hence with  $\text{O} = 15.879$  and  $\text{C} = 11.920$ ,

$$\text{Yt} = 88.943.$$

Ignoring the early work of Berzelius,† the determinations to be considered are those of Popp, Delafontaine, Bahr and Bunsen, Cleve, and Jones.

Popp‡ evidently worked with material not wholly free from earths of higher molecular weight than yttria. The yttrium sulphate was dehydrated at  $200^\circ$ ; the sulphuric acid was then estimated as barium sulphate, and after the excess of barium in the filtrate had been removed the yttrium was thrown down as oxalate and ignited to yield oxide. The following are the weights given by Popp:

<i>Sulphate.</i>	<i>BaSO<sub>4</sub>.</i>	<i>Yt<sub>2</sub>O<sub>3</sub>.</i>	<i>H<sub>2</sub>O.</i>
1.1805 gm.	1.3145 gm.	.4742 gm.	.255 gm.
1.4295 "	1.593 "	.5745 "	.308 "
.8455 "	.9407 "	.3392 "	.1825 "
1.045 "	1.1635 "	.4195 "	.2258 "

Eliminating water, these figures give us for the percentages of  $\text{Yt}_2\text{O}_3$  in  $\text{Yt}_2(\text{SO}_4)_3$  the values in column A. In column B I put the quantities of  $\text{Yt}_2\text{O}_3$  proportional to 100 parts of  $\text{BaSO}_4$ :

A.	B.
51.237	36.075
51.226	36.064
51.161	36.058
51.209	36.055
Mean, 51.208, $\pm .011$	Mean, 36.063, $\pm .003$

From B,  $\text{Yt} = 101.54$ . The values in A will be combined with similar data from other experimenters.

\* Forhandlingar ved de Skandinaviske Naturforskere, 8, 452. 1860.

† Lehrbuch, V Aufl., 3, 1225.

‡ Ann. Chem. Pharm., 131, 179. 1854.

In 1865 Delafontaine\* published some results obtained from yttrium sulphate, the yttrium being thrown down as oxalate and weighed as oxide. In the fourth column I give the percentages of  $Yt_2O_3$  reckoned from the anhydrous sulphate:

<i>Sulphate.</i>	$Yt_2O_3$ .	$H_2O$ .	<i>Per cent. <math>Yt_2O_3</math>.</i>
.9545 grm.	.371 grm.	.216 grm.	50.237
2.485 "	.9585 "	.565 "	49.922
2.153 "	.827 "	.4935 "	49.834
<hr/>			
Mean, 49.998, $\pm$ .081			

In another paper† Delafontaine gives the following percentages of  $Yt_2O_3$  in dry sulphate. The mode of estimation was the same as before:

48.23
48.09
48.37
<hr/>
Mean, 48.23, $\pm$ .055

Bahr and Bunsen,‡ and likewise Cleve, adopted the method of converting dry yttrium oxide into anhydrous sulphate, and noting the gain in weight. Bahr and Bunsen give us the two following results. I add the usual percentage column:

$Yt_2O_3$ .	$Yt_2(SO_4)_3$ .	<i>Per cent. <math>Yt_2O_3</math>.</i>
.7266 grm.	1.4737 grm.	49.304
.7856 "	1.5956 "	49.235
		<hr/>
Mean, 49.2695, $\pm$ .0233		

Cleve's first results are published in a joint memoir by Cleve and Hoeglund,§ and are as follows:

$Yt_2O_3$ .	$Yt_2(SO_4)_3$ .	<i>Per cent. <math>Yt_2O_3</math>.</i>
1.4060 grm.	2.8925 grm.	48.608
1.0930 "	2.2515 "	48.545
1.4540 "	2.9895 "	48.637
1.3285 "	2.7320 "	48.627
2.3500 "	4.8330 "	48.624
2.5780 "	5.3055 "	48.591
		<hr/>
Mean, 48.605, $\pm$ .0096		

In a later paper Cleve|| gives syntheses of yttrium sulphate made with yttria, which was carefully freed from terbia. The weights and percentages are as follows:

\* Ann. Chem. Pharm., 134, 108. 1865.

† Arch. Sci. Phys. et Nat. (2), 25, 119. 1866.

‡ Ann. Chem. Pharm., 137, 21. 1866.

§ K. Svenska Vet. Akad. Handlingar, Bd. 1, No. 8. 1873.

|| K. Svenska Vet. Akad. Handlingar, No. 9, 1882. See also Bull. Soc. Chim., 39, 120. 1883.



$Yt_2O_3$ .	$Yt_2(SO_4)_3$ .	<i>Per cent. <math>Yt_2O_3</math>.</i>
.8786	1.8113	48.507
.8363	1.7234	48.526
.8906	1.8364	48.497
.7102	1.4645	48.494
.7372	1.5194	48.519
.9724	2.0047	48.506
.9308	1.9197	48.487
.8341	1.7204	48.483
1.0224	2.1073	48.517
.9384	1.9341	48.519
.9744	2.0093	48.494
1.5314	3.1586	48.484

Mean, 48.503,  $\pm .0029$

Hence  $Yt = 88.449$ .

The yttria studied by Jones\* had been purified by Rowland's method—that is, by precipitation with potassium ferrocyanide—and certainly contained less than one-half of one per cent. of other rare earths as possible impurities. Two series of determinations were made—one by ignition of the sulphate, the other by its synthesis. The results were as follows, with the usual percentage column added:

*First Series. Syntheses.*

$Yt_2O_3$ .	$Yt_2(SO_4)_3$ .	<i>Per cent. <math>Yt_2O_3</math>.</i>
.2415	.4984	48.455
.4112	.8485	48.462
.2238	.4617	48.473
.3334	.6879	48.466
.3408	.7033	48.457
.3418	.7049	48.489
.2810	.5798	48.465
.3781	.7803	48.456
.4379	.9032	48.483
.4798	.9901	48.460

Mean, 48.467,  $\pm .0025$

*Second Series. Analyses.*

$Yt_2(SO_4)_3$ .	$Yt_2O_3$ .	<i>Per cent. <math>Yt_2O_3</math>.</i>
.5906	.2862	48.459
.4918	.2383	48.455
.5579	.2705	48.485
.6430	.3117	48.478
.6953	.3369	48.454
1.4192	.6880	48.478
.8307	.4027	48.477
.7980	.3869	48.484
.8538	.4139	48.477
1.1890	.5763	48.469

Mean, 48.472,  $\pm .0024$

\* Amer. Chem. Journ., 17, 154. 1895.

From syntheses.....	Yt = 88.287
From analyses.....	" = 88.309

These data of Jones were briefly criticised by Delafontaine,\* who regards a lower value as more probable. In a brief rejoinder† Jones defended his own work; but neither the attack nor the reply needs farther consideration here. They are referred to merely as part of the record.

For the percentage of yttria in the sulphate we now have eight series of determinations, to be combined in the usual way:

Popp.....	51.208,	± .0110
Delafontaine, first. . . . .	49.998,	± .0810
Delafontaine, second.....	48.230,	± .0550
Bahr and Bunsen. . . . .	49.2695,	± .0233
Cleve, earlier.....	48.605,	± .0096
Cleve, later.....	48.503,	± .0029
Jones, syntheses.....	48.467,	± .0025
Jones, analyses.....	48.472,	± .0024
<hr/>		
General mean.....	48.532,	± .0015

Hence, if  $O = 15.879$ ,  $\pm .0003$ , and  $S = 31.828$ ,  $\pm .0015$ ,

$$Yt = 88.580, \pm .0053.$$

If  $O = 16$ ,  $Yt = 89.255$ .

If only the four series by Cleve and by Jones are considered, the mean percentage of yttria in the sulphate becomes 48.481. Hence  $Yt = 88.350$ , or, with  $O = 16$ , 89.023.

This result is preferable to that derived from all the data, for it throws out determinations which are certainly erroneous. Cleve's early series might also be rejected, but its influence is insignificant.

---

\* Chem. News, 71, 243.

† Chem. News, 71, 305.

## SAMARIUM, GADOLINIUM, ERBIUM, AND YTTERBIUM.

The data relative to the atomic weights of these rare elements are rather scanty, and all depend upon analyses or syntheses of the sulphates.

## SAMARIUM.

Atomic weight given by Marignac,\* without details, as 149.4, and by Brauner,† as 150.7 in maximum. The first regular series of determinations was by Cleve,‡ who effected the synthesis of the sulphate from the oxide. Data as follows:

$Sm_2O_3$ .	$Sm_2(SO_4)_3$ .	<i>Per cent.</i> $Sm_2O_3$ .
1.6735	2.8278	59.180
1.9706	3.3301	59.175
1.1122	1.8787	59.201
1.0634	1.7966	59.190
.8547	1.4440	59.190
.7447	1.2583	59.183

Mean, 59.1865,  $\pm .0025$

Hence Sm = 149.038.

Another set of determinations by Bettendorff,§ after the same general method, gave as follows:

$Sm_2O_3$ .	$Sm_2(SO_4)_3$ .	<i>Per cent.</i> $Sm_2O_3$ .
1.0467	1.7675	59.219
1.0555	1.7818	59.238
1.0195	1.7210	59.225

Mean, 59.227,  $\pm .0038$

Hence Sm = 149.328.

Combining the two series, we have—

Cleve.....	59.1865, = .0025
Bettendorff.....	59.227, $\pm .0038$
General mean.....	59.199, $\pm .0021$

Hence, if  $SO_3 = 79.465$ ,  $\pm .00175$ ,

$$Sm = 149.127, \pm .0115.$$

If O = 16, Sm = 150.263.

According to Demarçay,|| samaria contains an admixed earth whose properties are yet to be described.

\* Arch. Sci. Phys. et Nat. (3), 3, 435. 1880.

† Journ. Chem. Soc., June, 1883.

‡ Journ. Chem. Soc., August, 1883. Compt. Rend., 97, 94.

§ Ann. Chem. Pharm., 263, 164. 1891.

|| Compt. Rend., 122, 728. 1896.

## GADOLINIUM.

This element, discovered by Marignac, must not be confounded with the mixture of metals from the gadolinite earths to which Nordenskiöld gave the same name. Several determinations of its atomic weight have been made, but Bettendorff's only were published with proper details.\* He effected the synthesis of the sulphate from the oxide, and his weights were as follows. The percentage of  $Gd_2O_3$  in  $Gd_2(SO_4)_3$  is given in the third column:

$Gd_2O_3$ .	$Gd_2(SO_4)_3$ .	<i>Per cent.</i> $Gd_2O_3$ .
1.0682	1.7779	60.082
1.0580	1.7611	60.076
1.0796	1.7969	60.081

Mean, 60.080,  $\pm$  .0013

Hence, with  $SO_3 = 79.465$ ,  $Gd = 155.575$ .

If  $O = 16$ ,  $Gd = 156.761$ .

Boisbaudran† found  $Gd = 155.33$ , 156.06, 155.76, and 156.12. The last he considers the best, but gives no details as to antecedent values. He also quotes Marignac, who found  $Gd = 156.75$ , and Cleve, who found 154.15, 155.28, 155.1, and 154.77. Probably these all depend upon  $SO_3 = 80$ .

## ERBIUM.

Since the earth which was formerly regarded as the oxide of this metal is now known to be a mixture of two or three different oxides, the older determinations of its molecular weight have little more than historical interest. Nevertheless the work done by several investigators may properly be cited, since it sheds some light upon certain important problems.

First, Delafontaine's‡ early investigations may be considered. A sulphate, regarded as erbium sulphate, gave the following data. An oxalate was thrown down from it, which, upon ignition, gave oxide. The percentages in the fourth column refer to the anhydrous sulphate. In the last experiment water was not estimated, and I assume for its water the mean percentage of the four preceding experiments:

<i>Sulphate.</i>	$Er_2O_3$ .	$H_2O$ .	<i>Per cent.</i> $Er_2O_3$ .
.827 grm.	.353 grm.	.177 grm.	54.308
1.0485 "	.4475 "	.226 "	54.407
.803 "	.3415 "	.171 "	54.035
1.232 "	.523 "	.264 "	54.028
1.1505 "	.495 "	.....	54.760

Mean, 54.308,  $\pm$  .0915

Hence  $Er = 117.86$ .

\* Ann. Chem. Pharm., 270, 376. 1892.

† Compt. Rend., 111, 409. 1890.

‡ Ann. Chem. Pharm., 134, 108. 1865.

Bahr and Bunsen\* give a series of results, representing successive purifications of the earth which was studied. The final result, obtained by the conversion of oxide into sulphate, was as follows:

.7870 grm. oxide gave 1.2765 grm. sulphate. 61.653 per cent. oxide.

Hence  $\text{Er} = 167.82$ .

Hoeglund,† following the method of Bahr and Bunsen, gives these results:

$\text{Er}_2\text{O}_3$ .	$\text{Er}_2(\text{SO}_4)_3$ .	Per cent. $\text{Er}_2\text{O}_3$ .
1.8760 grm.	3.0360 grm.	61.792
1.7990 "	2.9100 "	61.821
2.8410 "	4.5935 "	61.848
1.2850 "	2.0775 "	61.853
1.1300 "	1.827 "	61.850
.8475 "	1.370 "	61.861

Mean, 61.8375,  $\pm .0063$

Hence  $\text{Er} = 169.33$ .

According to Thalén,‡ spectroscopic evidence shows that the "erbia" studied by Hoeglund was largely ytterbia.

Humpidge and Burney§ give data as follows:

1.9596 grm. $\text{Er}_2(\text{SO}_4)_3$ gave	1.2147 grm. $\text{Er}_2\text{O}_3$ .	61.987 per cent.
1.9011 "	1.1781 "	61.965 "

Mean, 61.976,  $\pm .0074$

Hence  $\text{Er} = 170.46$ .

The foregoing data were all published before the composite nature of the supposed erbia was fully recognized. It will be seen, however, that three sets of results were fairly comparable, while Delafontaine evidently studied an earth widely different from that investigated by the others. Since the discovery of ytterbium, some light has been thrown on the matter. The old erbia is a mixture of several earths, to one of which, a rose-colored body, the name erbia is now restricted. For the atomic weight of the true erbium Cleve|| gives three determinations, based on syntheses of the sulphate after the usual method. His weights were as follows, with the percentage ratio added:

$\text{Er}_2\text{O}_3$ .	$\text{Er}_2(\text{SO}_4)_3$ .	Per cent. $\text{Er}_2\text{O}_3$ .
1.0692	1.7436	61.321
1.2153	1.9820	61.317
.7850	1.2808	61.290

Mean, 61.309,  $\pm .0068$

Hence, with  $\text{SO}_3 = 79.465$ ,  $\text{Er} = 165.059$ .

If  $\text{O} = 16$ ,  $\text{Er} = 166.316$ .

\* Ann. Chem. Pharm., 137, 21. 1866.

† K. Svenska Vet. Akad. Handlingar, Bd. 1, No. 6.

‡ Wiedemann's Beiblätter, 5, 122. 1881.

§ Journ. Chem. Soc., Feb., 1879, p. 116.

|| K. Svensk. Vet. Akad. Handlingar, No. 7, 1880. Abstract in Compt. Rend., 91, 352.

It is not worth while to combine this result with the earlier determinations, for they are now worthless.

## YTTERBIUM.

For ytterbium we have one very good set of determinations by Nilson.\* The oxide was converted into the sulphate after the usual manner:

$Yb_2O_3$ .	$Yb_2(SO_4)_3$ .	Per cent. $Yb_2O_3$ .
1.0063 gm.	1.6186 gm.	62.171
1.0139 "	1.6314 "	62.149
.8509 "	1.3690 "	62.155
.7371 "	1.1861 "	62.145
1.0005 "	1.6099 "	62.147
.8090 "	1.3022 "	62.126
1.0059 "	1.6189 "	62.134

Mean, 62.147,  $\pm$  .0036

Hence, with  $SO_3 = 79.465$ ,  $Yb = 171.880$ .

If  $O = 16$ ,  $Yb = 173.190$ .

## TERBIUM, THULIUM, HOLMIUM, DYSPROSIUM, ETC.

For these elements the data are both scanty and vague. Concerning the atomic weights of holmium and dysprosium, practically nothing has been determined. To thulium, Cleve † assigns a value of  $Tm = 170.7$ , approximately, but with no details as to weighings. Probably the value was computed with  $SO_3 = 80$ .

For terbium, ignoring older determinations, Lecoq de Boisbaudran has published two separate estimates.‡ First, for two preparations, one with a lighter and one with a darker earth, he gives  $Tb = 161.4$  and  $163.1$  respectively. In his second paper he gives  $Tb = 159.01$  to  $159.95$ . These values probably are all referred to  $SO_3 = 80$ .

\* Compt. Rend., 91, 56. 1880. Berichte, 13, 1430.

† Compt. Rend., 91, 329. 1880.

‡ Compt. Rend., 102, 396, and 111, 474.

## ARGON AND HELIUM.

The true atomic weights of these remarkable gases are still in doubt, and so far can only be inferred from their specific gravities.

For argon, the discoverers, Rayleigh and Ramsay,\* give various determinations of density, ranging, with hydrogen taken as unity, from 19.48 to 20.6. In an addendum to the same paper, Ramsay alone gives for the density of argon prepared by the magnesium method the mean value of 19.941. In a later communication † Rayleigh gives determinations made with argon prepared by the oxygen method, and puts the density at 19.940.

For the density of helium, Ramsay ‡ gets 2.18, while Langlet § finds the somewhat lower value 2.00.

From one set of physical data both gases appear to be monatomic, but from other considerations they are supposably diatomic. Upon this question controversy has been most active, and no final settlement has yet been reached. If diatomic, argon and helium have approximately the atomic weights two and twenty respectively; if monatomic, these values must be doubled. In either case helium is an element lying between hydrogen and lithium, but argon is most difficult to classify. With the atomic weight 20, argon falls in the eighth column of the periodic system between fluorine and sodium, but if it is 40 the position of the gas is anomalous. A slightly lower value would place it between chlorine and potassium, and again in the eighth column of Mendelejeff's table; but for the number 40 no opening can be found.

It must be noted that neither gas, so far, has been proved to be absolutely homogeneous, and it is quite possible that both may contain admixtures of other things. This consideration has been repeatedly urged by various writers. If argon is monatomic, a small impurity of greater density, say of an unknown element falling between bromine and rubidium, would account for the abnormality of its atomic weight, and tend towards the reduction of the latter. If the element is diatomic, its classification is easy enough on the basis of existing data. Its resemblances to nitrogen, as regards density, boiling point, difficulty of liquefaction, etc., lead me personally to favor the lower figure for its atomic weight, and the same considerations may apply to helium also. Until further evidence is furnished, therefore, I shall assume the values two and twenty as approximately true for the atomic weights of helium and argon.

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\* Phil. Trans., 186, pp. 220 to 223, and 238. 1895.

† Chem. News, 73, 75. 1896.

‡ Journ. Chem. Soc., 1895, p. 684.

§ Zeitsch. Anorg. Chem., 10, 289. 1895.

## TABLE OF ATOMIC WEIGHTS.

The following table contains the values for the various atomic weights found or adopted in the preceding calculations. As the table is intended for practical use, the figures are given only to the second decimal, the third being rarely, if ever, significant. In most cases even the first decimal is uncertain, and in some instances whole units may be in doubt.

	H = 1.	O = 16.
Aluminum . . . . .	26.91	27.11
Antimony . . . . .	119.52	120.43
Argon . . . . .	?	?
Arsenic. . . . .	74.44	75.01
Barium . . . . .	136.39	137.43
Bismuth. . . . .	206.54	208.11
Boron . . . . .	10.86	10.95
Bromine. . . . .	79.34	79.95
Cadmium . . . . .	111.10	111.95
Cæsium. . . . .	131.89	132.89
Calcium . . . . .	39.76	40.07
Carbon . . . . .	11.92	12.01
Cerium . . . . .	139.10	140.20
Chlorine . . . . .	35.18	35.45
Chromium . . . . .	51.74	52.14
Cobalt. . . . .	58.49	58.93
Columbium. . . . .	93.02	93.73
Copper . . . . .	63.12	63.60
Erbium . . . . .	165.06	166.32
Fluorine . . . . .	18.91	19.06
Gadolinium. . . . .	155.57	156.76
Gallium. . . . .	69.38	69.91
Germanium. . . . .	71.93	72.48
Glucinum . . . . .	9.01	9.08
Gold . . . . .	195.74	197.23
Helium . . . . .	?	?
Hydrogen. . . . .	1.000	1.008
Indium . . . . .	112.99	113.85
Iodine . . . . .	125.89	126.85
Iridium. . . . .	191.66	193.12
Iron. . . . .	55.60	56.02
Lanthanum. . . . .	137.59	138.64
Lead . . . . .	205.36	206.92
Lithium . . . . .	6.97	7.03
Magnesium. . . . .	24.10	24.28
Manganese . . . . .	54.57	54.99
Mercury . . . . .	198.49	200.00
Molybdenum . . . . .	95.26	95.99
Neodymium . . . . .	139.70	140.80
Nickel . . . . .	58.24	58.69



	H = 1.	O = 16.
Nitrogen.....	13.93	14.04
Osmium.....	189.55	190.99
Oxygen.....	15.88	16.00
Palladium.....	105.56	106.36
Phosphorus.....	30.79	31.02
Platinum.....	193.41	194.89
Potassium.....	38.82	39.11
Praseodymium.....	142.50	143.60
Rhodium.....	102.23	103.01
Rubidium.....	84.78	85.43
Ruthenium.....	100.91	101.68
Samarium.....	149.13	150.26
Scandium.....	43.78	44.12
Selenium.....	78.42	79.02
Silicon.....	28.18	28.40
Silver.....	107.11	107.92
Sodium.....	22.88	23.05
Strontium.....	86.95	87.61
Sulphur.....	31.83	32.07
Tantalum.....	181.45	182.84
Tellurium.....	126.52	127.49
Terbium.....	158.80	160.00
Thallium.....	202.61	204.15
Thorium.....	230.87	232.63
Thulium.....	169.40	170.70
Tin.....	118.15	119.05
Titanium.....	47.79	48.15
Tungsten.....	183.43	184.83
Uranium.....	237.77	239.59
Vanadium.....	50.99	51.38
Ytterbium.....	171.88	173.19
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Zinc.....	64.91	65.41
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SMITHSONIAN MISCELLANEOUS COLLECTIONS

1084

# BIBLIOGRAPHY OF THE METALS OF THE PLATINUM GROUP

PLATINUM, PALLADIUM,  
IRIDIUM, RHODIUM, OSMIUM, RUTHENIUM

1748-1896

BY  
JAS. LEWIS HOWE



CITY OF WASHINGTON  
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1897



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## LETTER OF TRANSMITTAL.

WASHINGTON, January 18th, 1897.

The Committee of the American Association for the Advancement of Science having charge of Indexing Chemical Literature has voted to recommend to the Smithsonian Institution for publication the following: "A Bibliography of the Metals of the Platinum Group, 1748-1896," by Prof. Jas. Lewis Howe, M. D., Ph. D.

H. CARRINGTON BOLTON, *Chairman.*

MR. S. P. LANGLEY,

*Secretary of the Smithsonian Institution.*



## PREFACE.

The purpose of this Bibliography is to enumerate the articles upon the metals of the platinum group found in scientific literature to the close of the year 1896. It is sought to make the record of the chemistry of these metals as complete as possible, and it is believed that few references of importance are omitted. Chloroplatinates of organic bases are considered only in the case of those early formed. Outside of the department of chemistry several divisions of the subject have not been followed beyond the earlier references, *e. g.*, the use of platinum in electrical apparatus, in photography, and in connection with the X-rays. To facilitate the use of the indexes the number of each title includes the year. The first reference is that of the original article. The abbreviations used are generally those recommended by the Committee on Bibliography of the American Association for the Advancement of Science.

After having been engaged on this work for some time, the compiler obtained a copy of the pamphlet "Fragment einer Monographie des Platins und der Platinmetalle," by C. Claus. This was published in 1883 by the St. Petersburg Académie des Sciences, from papers found after Professor Claus' death, which had occurred more than twenty years before. But three hundred copies of the pamphlet were printed and it is very rare. Among other material it contains a quite complete bibliography of the platinum metals, brought down to 1861, but unfortunately, owing probably to the illegibility of the manuscript, it suffers from very many errors. It is a critical bibliography and hence, owing to the author's unique knowledge of the platinum metals, is very valuable.

Much of the work on this Bibliography has been done in the Library of the American Academy of Arts and Sciences and in that of the Massachusetts Institute of Technology, and the compiler is greatly indebted for the facilities offered him at both these places. Especially valuable was the assistance rendered by Dr. Holden, the Librarian of the Academy. He would also gratefully acknowledge the aid received from his former

pupil, Miss M. M. Tevis, from Dr. H. Carrington Bolton, Professor T. H. Norton of the University of Cincinnati, Professor H. P. Talbot of the Institute of Technology, and many others who cannot be enumerated. Dr. Bolton's invaluable Catalogue of Scientific Periodicals and the Royal Society Catalogue have been freely used and of great help in the verification of data.

JAS. LEWIS HOWE.

Washington and Lee University, Lexington, Va.,  
December, 1896.

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# BIBLIOGRAPHY OF METALS OF THE PLATINUM GROUP:

PLATINUM, PALLADIUM, IRIDIUM, RHODIUM, OSMIUM,  
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1748-1896.

BY JAS. LEWIS HOWE.

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- 1810: 3. L. N. VAUQUELIN. Analyse du platine trouvé à Saint-Domingue. Pt.  
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- 1810: 4. H. DAVY. Researches on the oxymuriatic acid, its nature and combinations, etc. (Action of platinum on aqua regia.) Pt.  
Phil. Trans. London, 100 (1810), 243; Ann. d. Chim. 76 (1810), 134;  
J. für Chem. (Schweigger), 3 (1811), 110; Bibl. Brit. 45 (1810),  
229; Ann. der Phys. (Gilbert), 39 (1811), 3; Brugnatelli, Giornale,  
4 (1811), 129; J. de Phys. 71 (1810), 326.
- 1810: 5. ———. Fusion of iridium and osmium at the Royal In-  
stitution. (Note on lecture.) Ir, Os.  
Phil. Mag. 35 (1810), 463.
- 1811: 1. A. F. GEHLEN. Platinum und Palladium in Brasilien und St.  
Domingo gefunden. (Resumé.) Pt, Pd, Rh, Ir, Os.  
J. für Chem. (Schweigger), 1 (1811), 362.
- 1811: 2. A. VON HUMBOLDT. Essai politique sur le royaume de la  
Nouvelle-Espagne. (Sur les mines du Mexique.) Pt.  
J. des Mines, 29 (1811), 101.
- 1811: 3. H. DAVY. Elements of chemical philosophy. (Expansion of  
platinum and palladium, melting of platinum in electric light,  
oxids of platinum and palladium and sulfid of palladium.) Pt, Pd.  
J. für Chem. (Schweigger), 8 (1813), 336, 342; Phil. Mag. 40 (1812),  
442.
- 1811: 4. H. DAVY. On some of the combinations of oxymuriatic gas  
and oxygene. (Action of alkalies on platinum.) Pt.  
Phil. Trans. London, 101 (1811), 1; Proc. Roy. Soc. London, 1  
(1832), 385; J. für Chem. (Schweigger), 3 (1811), 209, 212, 232;  
Ann. d. Chim. 78 (1811), 298; 79 (1811), 5; Ann. der Phys. (Gil-  
bert), 39 (1811), 43; J. de Phys. 72 (1811), 358; Nicholson's J.  
29 (1811), 222.
- 1811: 5. G. DE MORVEAU. De la platinure et du doublé ou plaqué de  
platine. (Plating with platinum.) Pt.  
Ann. d. Chim. 77 (1811), 297; J. des Mines, 29 (1811), 392; Nichol-  
son's J. 30 (1812), 292; Brugnatelli, Giornale, 4 (1811), 356.
- 1811: 6. M. E. CHEVREUL. Recherches chimiques sur le bois de  
Campèche. (Precipitation of albumen by iridium chlorid.) Ir.  
Ann. Mus. Nat. Hist. Paris. 17 (1811), 339; J. für Chem. (Schweig-  
ger), 8 (1813), 290; Ann. d. Chim. 81 (1812), 158; Bull. de Pharm.  
3 (1811), 546; Ann. der Phys. (Gilbert), 42 (1812), 145.
- 1812: 1. P. JOHNSON. Experiments which prove platina, when com-  
bined with gold and silver, to be soluble in nitric acid. Pt.  
Phil. Mag. 40 (1812), 3.
- 1812: 2. E. DAVY. On the combinations of sulphur and phosphorus  
with platina. Pt.  
Phil. Mag. 40 (1812), 27; J. für Chem. (Schweigger), 10 (1814), 382.

- 1812: 3. E. DAVY. On some new combinations of platina. Pt.  
 With sulfur, p. 209.  
 With phosphorus, oxygen, chlorin, ammonia, p. 263.  
 With sulfuric acid, potassium sulfate, sodium sulfate, &c., p. 350.  
 Fulminating platina, p. 361.  
 Phil. Mag. 40 (1812), 209, 263, 350.
- 1812: 4. J. J. BERZELIUS. Försök till ett rättfärdigande af de theoretiskt-chemiska åsigter. (Oxids and sulfids of the platinum metals.) Pt, Pd, Ir, Os, Rh.  
 Kong. Vet. Acad. Handl. Stockholm, 33 (1813), 175, 196, 204; Ann. of Phil. (Thomson), 3 (1813), 252, 353; 5 (1815), 20; J. für Chem. (Schweigger), 7 (1813), 55, 66; Ann. d. Chim. 83 (1812), 167, 168; 87 (1813), 126, 138.
- 1813: 1. L. N. VAUQUELIN. Mémoire sur le palladium et le rhodium. (History, separation, properties, compounds.) (Best resumé of the history of palladium.) Pd, Rh.  
 Ann. d. Chim. 88 (1813), 167; Ann. of Phil. (Thomson), 4 (1814), 216, 271, 308; 5 (1815), 21; J. für Chem. (Schweigger), 12 (1814), 265; Phil. Mag. 44 (1814), 33; Brugnatelli, Giornale, 8 (1815), 221.
- 1813: 2. LEITHNER. (Process of rendering platinum malleable.) Pt.  
 Ann. of Phil. (Thomson), 5 (1815), 20.
- 1813: 3. A. F. GEHLEN. Ueber ein neues Verfahren das Platin zum Verarbeiten geschickt zu machen. Pt.  
 J. für Chem. (Schweigger), 7 (1813), 309.
- 1813: 4. J. S. C. SCHWEIGGER. Ueber Leithner's Verfahren Platin zum Verarbeiten geschickt zu machen. Pt.  
 J. für Chem. (Schweigger), 7 (1813), 514.
- 1813: 5. W. H. WOLLASTON. A method of drawing extremely fine wires. Pt.  
 Phil. Trans. London, 103 (1813), 114; Proc. Roy. Soc. London, 1 (1832), 455; Ann. of Phil. (Thomson), 1 (1813), 224; Ann. der Phys. (Gilbert), 52 (1816), 284; Bibl. Brit. [2], 1 (1816), 119.
- 1813: 6. [K. A.] NEUMANN. Bemerkungen über Platingefässe. Pt.  
 J. für Chem. (Schweigger), 9 (1813), 213.
- 1813: 7. A. MARCET. On an easy method of procuring a very intense heat. Pt.  
 Ann. of Phil. (Thomson), 2 (1813), 99; J. für Chem. (Schweigger), 11 (1814), 45; Brugnatelli, Giornale, 7 (1814), 230.



- 1813: 8. F. C. VOGEL. Beiträge zu der Lehre von den bestimmten chemischen Mischungs-Verhältnissen. (Oxids of platinum and palladium and platinum amalgam.) Pt, Pd.  
J. für Chem. (Schweigger), 7 (1813), 188.
- 1814: 1. L. N. VAUQUELIN. Mémoire sur l'Iridium et sur l'Osmium. (History, obtaining, properties, compounds, alloys.) Ir, Os, Pt.  
Ann. d. Chim. 89 (1814), 150, 225; J. für Chem. (Schweigger), 24 (1818), 21; Ann. of Phil. (Thomson), 6 (1815), 433; Hermbstädt, Museum, 6 (1815), 83.
- 1814: 2. L. N. VAUQUELIN. Sur le palladium et le rhodium. Pd, Rh.  
J. des Mines, 35 (1814), 141, from Nouv. Bul. des Sc.; J. für Chem. (Schweigger), 12 (1814), 265; Ann. of Phil. (Thomson), 4 (1814), 216, 271; Phil. Mag. 44 (1814), 33.
- 1814: 3. A. LAUGIER. Nouvelle manière de retirer l'Osmium du platine brut. Os.  
Ann. d. Chim. 89 (1814), 191; J. für Chem. (Schweigger), 19 (1817), 70; Phil. Mag. 44 (1814), 51.
- 1814: 4. L. N. VAUQUELIN. Expériences sur le muriate d'Iridium et de potasse. Ir.  
Ann. d. Chim. 90 (1814), 260.
- 1814: 5. R. L. RUHLAND. Beiträge zur Geschichte des Iods. (Verbindung des Iods mit Platin.) Pt.  
J. für Chem. (Schweigger), 11 (1814), 137; München, Denkschriften, 1814-15, 151.
- 1814: 6. J. S. C. SCHWEIGGER. Amalgamiren des Platins mittelst des electrischen Stromes. Pt.  
J. für Chem. (Schweigger), 12 (1814), 224.
- 1814: 7. J. P. J. D'ARCET. Note sur l'essai des alliages de platine et d'argent. Pt.  
Ann. d. Chim. 89 (1814), 135.
- 1814: 8. W. A. LAMPADIUS. Legirung des Nickels und Platins. Pt.  
J. für Chem. (Schweigger), 10 (1814), 175; Ann. of Phil. (Thomson), 5 (1815), 61.
- 1814: 9. J. W. DÖBEREINER. Ueber Platinagefäße (besonders in Paris zu chemischem Gebrauche verfertigte) und Bemerkungen über das Verhalten der Salpetersauren Alkalien gegen Platin und über Kali. Pt.  
J. für Chem. (Schweigger), 10 (1814), 217.
- 1814: 10. JORIS. Ueber Verfertigung von Platingefäßen. Ausbesserung schadhaft gewordener, und über eine Gedächtnismünze aus Platin auf den Sieg bei Leipzig. Pt.  
J. für Chem. (Schweigger), 11 (1814), 385.

- 1814: 11. SCHOLZ. Ueber Platinaverarbeitung. Pt.  
J. für Chem. (Schweigger), 12 (1814), 349.
- 1815: 1. L. N. VAUQUELIN. Note sur la manière d'obtenir le muriate ammoniac de rhodium, régulièrement cristallisé. Rh.  
Ann. d. Chim. 93 (1815), 204.
- 1815: 2. J. G. CHILDREN. Experiments with a large voltaic battery. Pt, Ir, Os.  
(Fusion of platinum, &c.)  
Phil. Trans. London, 105 (1815), 363; Ann. d. Chim. 96 (1815), 120;  
Brugnatelli, Giornale, 9 (1816), 282; Ann. der Phys. (Gilbert),  
52 (1816), 353; J. für Chem. (Schweigger), 16 (1816), 355.
- 1816: 1. C. RIDOLFI. (Purification of platinum.) Pt.  
Giornale di Scienza ed Arti (Firenze); Quart. J. Sci. 1 (1816),  
259; Ann. of Phil. (Thomson), 7 (1817), 29; 13 (1819), 70; J. für  
Chem. (Schweigger), 24 (1818), 439; Phil. Mag. 48 (1816), 72;  
53 (1819), 68; Bibl. Brit. [2], 2 (1816), 73.
- 1816: 2. CHAUDET. Mémoire sur quelques expériences tendantes à  
déterminer par la coupellation . . . le titre exact d'un lingot con-  
tenant de l'or, du platine, de l'argent et du cuivre. Pt.  
Ann. chim. phys. 2 (1816), 264; Karsten, Archiv f. Bergbau, 11  
(1826), 66; Ann. des Mines, 2 (1817), 105.
- 1816: 3. J. P. DESSAIGNES. Phénomènes de répulsion et d'attraction  
sans électricité. (Platinum plates in evening air by window  
attract and repel needle.) Pt.  
J. de Phys. 83 (1816), 15; J. für Chem. (Schweigger), 20 (1817), 86.
- 1817: 1. A. VON HUMBOLDT. Ueber die Höhe von Bergen in Hindostan.  
(Occurrence of platinum in South America, p. 31.) Pt.  
Ann. der Phys. (Gilbert), 56 (1817), 1.
- 1817: 2. L. N. VAUQUELIN. Sur le sulfure de platine, sur ses oxides,  
et quelques combinaisons de ce métal. (Also on platinum  
chlorid.) Pt.  
Ann. chim. phys. 5 (1817), 260; J. für Chem. (Schweigger), 20  
(1817), 394, 398; J. de Phys. 85 (1817), 21, 113, 355; Ann. of Phil.  
(Thomson), 12 (1818), 18; Quart. J. Sci. 4 (1818), 74; N. J. der  
Pharm. (Trommsd.), 2 (1818), 325; Ann. des Mines, 3 (1818), 195.
- 1817: 3. L. N. VAUQUELIN. Sur quelques sels triples de platine, et  
notamment sur le muriate de ce métal et de soude. (Also on  
platinum sulfate.) Pt.  
Ann. chim. phys. 5 (1817), 392; J. für Chem. (Schweigger), 20  
(1817), 451; Ann. of Phil. (Thomson), 12 (1818), 28; Ann. des  
Mines, 3 (1818), 195.

- 1817: 4. A. F. GEHLEN. Ueber die Reduction der Metalle durch einander, und die dabei stattfindenden Licht-Erscheinungen. (Action of platinum on arsenious oxid, iron, copper, zine, &c., p. 356.) Pt.  
J. für Chem. (Schweigger), 20 (1817), 353.
- 1817: 5. E. DAVY. On a new fulminating platinum. Pt.  
Phil. Trans. 107 (1817), 136; Proc. Roy. Soc. London, 2 (1833), 63; Ann. of Phil. (Thomson), 7 (1816), 468; 9 (1817), 229; Ann. chim. phys. 5 (1817), 413; J. für Chem. (Schweigger), 19 (1817), 91; Phil. Mag. 49 (1817), 146; Quart. J. Sci. 3 (1817), 131; Bibl. Brit. [2], 5 (1817), 160; 6 (1817), 155; Ann. des Mines, 3 (1818), 197.
- 1817: 6. T. VON GROTHUS. Beitrag zur Geschichte der Anthrazothionsäure. (Platinanthrazothionhydrat. p. 242.) Pt.  
J. für Chem. (Schweigger), 20 (1817), 225; Ann. of Phil. (Thomson), 13 (1819), 39.
- 1817: 7. H. A. VON VOGEL. Notiz über das Lithion. (Einwirkung von Lithion auf Platintiegeln.) Pt.  
J. für Chem. (Schweigger), 21 (1817), 345.
- 1817: 8. E. D. CLARKE. Account of some experiments made with Newman's blowpipe by inflaming a highly condensed mixture of the gaseous constituents of water. (Fusion and alloys of platinum metals.) Pt, Pd, Ir, Os, Rh.  
Quart. J. Sci. 2 (1817), 104; Ann. chim. phys. 3 (1816), 39; Ann. des Mines, 1 (1816), 453; Ann. der Phys. (Gilbert), 55 (1817), 8, 119; J. für Chem. (Schweigger), 18 (1816), 239; Oken, Isis, 1, (1817), 956.
- 1817: 9. E. D. CLARKE. Further observations respecting the decomposition of earths, and other experiments made by burning a highly compressed mixture of the gaseous constituents of water. (Similar to above.) Pt, Pd, Ir, Os, Rh.  
Ann. of Phil. (Thomson), 9 (1817), 89, 194; Ann. der Phys. (Gilbert), 62 (1819), 339; J. für Chem. (Schweigger), 21 (1817), 385.
- 1817: 10. H. DAVY. Some new experiments and observations on the combustion of gaseous mixtures, with an account of a method of preserving a continued light in mixtures of inflammable gases and air without flame (by platinum and palladium). Pt, Pd.  
Phil. Trans. London, 107 (1817), 77; Proc. Roy. Soc. London, 2 (1833), 61; J. für Chem. (Schweigger), 20 (1817), 178; J. de Phys. 84 (1817), 225; Bibl. Brit. [2], 5 (1817), 319.
- 1817: 11. G. SCHÜBLER. Ueber das Entglühen erwärmter Metalle im Aetherdunst, etc. Pt, Pd.  
J. für Chem. (Schweigger), 20 (1817), 199; Bibl. Brit. [2], 5 (1817), 147.

- 1817: 12. M. F[ARADAY]. Report on some experiments made with compressed oxygene and hydrogen, in the laboratory of the Royal Institution. Pt.  
Quart. J. Sci. 2 (1817), 461; J. für Chem. (Schweigger), 18 (1816), 337.
- 1817: 13. J. MURRAY. On the phenomena of platinum and other wires in inflammable media. Pt.  
Phil. Mag. 49 (1817), 120, 142.
- 1817: 14. J. T. COOPER. On some combinations of platinum. (Alloys and oxids.) Pt.  
Quart. J. Sci. 3 (1817), 119.
- 1818: 1. H. HEULAND. On a mass of platinum at Madrid (from Chocó). Pt.  
Ann. of Phil. (Thomson), 12 (1818), 200; Phil. Mag. 52 (1818), 382; 57 (1821), 228; Ann. chim. phys. 9 (1818), 331.
- 1818: 2. J. MAWE. Nachricht von dem Vorkommen . . . edler Metalle in Brasilien. Pt, Ir, Os.  
Ann. der Phys. (Gilbert), 59 (1818), 168.
- 1818: 3. J. CLOUD. An account of some experiments made on crude platinum, and a new process for separating palladium and rhodium from that metal. Pt, Pd, Rh.  
Trans. Amer. Phil. Soc. [2], 1 (1818), 161; Ann. der Phys. (Gilbert), 72 (1822), 253; J. für Chem. (Schweigger), 43 (1825), 316; Bul. math. chim. (Férussac), 1 (1824), 313; Ann. des Mines, 4 (1819), 131; Berzelius Jsb. 3 (1824), 104.
- 1818: 4. F. ACCUM. A practical treatise on chemical reagents. London, 1818. (Palladium in platinum ore; precipitated by mercury prussiate and heat.) Pt, Pd.  
Bibl. Brit. [2], 9 (1818), 37.
- 1818: 5. J. J. BERZELIUS. Ueber das selenium. (No compound with rhodium, palladium or platinum.) Pt, Pd, Rh.  
J. für Chem. (Schweigger), 23 (1818), 439.
- 1818: 6. J. J. BERZELIUS. Försök att närmare bestämma åtskilliga oorganiska kroppars sammansättning, till vinnanda af en närmare utveckling af läran om de kemiska proportionerna. (Versuche über die Zusammensetzung der Rhodiumoxyde, und ihre Verhältnisse zu den Säuren.) Rh.  
Hisinger, Afhandl. Fysik, 5 (1818), 379; J. für Chem. (Schweigger), 23 (1818), 285; Ann. chim. phys. 11 (1819), 225; J. de Phys. 86 (1818), 356; Quart. J. Sci. 12 (1822), 321; Ann. of Phil. (Thomson), 15 (1820), 352.

- 1818: 7. J. J. BERZELIUS. Gewicht der elementaren Maasstheile.  
J. für Chem. (Schweigger), 22 (1818), 317, 325, 327. Pt, Pd, Rh.
- 1818: 8. A. J. FRÈRE DE MONTIZON. Observation sur le rapport qui  
existe entre l'oxidation des métaux et leur pesanteur spécifique.  
Ann. chim. phys. 7 (1818), 9. Pt, Pd.
- 1818: 9. J. CLOUD. An attempt to ascertain the fusing temperature of  
metals. Pt, Pd, Rh.  
Trans. Amer. Phil. Soc. [2], 1 (1818), 167.
- 1818: 10. J. J. PRECHTL. Schmelzung von Platin durch Ofenfeuer.  
Pt.  
Ann. der Phys. (Gilbert), 58 (1818), 111; Ann. of Phil. (Thomson), 13 (1819), 229; Bibl. Brit. [2], 11 (1819), 80; Ann. des Mines, 4 (1819), 130.
- 1818: 11. L. N. VAUQUELIN. Note sur une nouvelle espèce d'alcali  
mineral (lithion). (Action of lithia on platinum.) Pt.  
Ann. chim. phys. 7 (1818), 287; Ann. des Mines, 3 (1818), 119; J.  
für Chem. (Schweigger), 21 (1817), 450.
- 1818: 12. L. J. GAY-LUSSAC. Sur la fixité du degré d'ébullition des  
liquides. (Use of platinum wire to prevent "bumping.") Pt.  
Ann. chim. phys. 7 (1818), 313; J. für Chem. (Schweigger), 24  
(1818), 327; Ann. of Phil. (Thomson), 12 (1818), 129.
- 1818: 13. S. T. VON SÖMMERRING. Glühung des Platins über Alcohol.  
(Experiment before the Acad. of Sci., München.) Pt.  
J. für Chem. (Schweigger), 22 (1818), 228.
- 1818: 14. P. ERMAN. Ueber eine eigenthümliche reziproke Wirkung  
der zwei entgegengesetzten elektrischen Thätigkeiten. (Action of  
the incandescent platinum of Davy's aphlogistic lamp.) Pt.  
Abhandl. Akad. Berlin. 1818-'19, 351; Ann. chim. phys. 25 (1824),  
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- 1818: 15. T. GILL. On a lamp without a flame. Pt.  
Ann. of Phil. (Thomson), 11 (1818), 217; Amer. J. of Sci. 1 (1819),  
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- 1818: 16. H. DAVY. On an ignited wire lamp. Pt.  
Quart. J. Sci. 5 (1818), 128; Amer. J. of Sci. 1 (1819), 309; Phil.  
Mag. 50 (1817), 230.
- 1818: 17. ———. Emploi du camphre pour tenir un fil de platine  
rouge. (Observation of H. Davy.) Pt.  
Ann. chim. phys. 8 (1818), 443.

- 1818: 18. P. L. DULONG and A. T. PETIT. Recherches sur la mesure des temperatures. (Specific heat of platinum, p. 148.) Pt.  
Ann. chim. phys. 7 (1818), 113; J. für Chem. (Schweigger), 25 (1819), 322; Ann. of Phil. (Thomson), 13 (1819), 167; Ann. der Phys. (Gilbert), 58 (1818), 254; J. de Phys. 82 (1818), 313; J. Ecole Polyt. Paris, 11 (1820), 189.
- 1819: 1. J. J. BERZELIUS. Examination of some compounds which depend upon very weak affinities. (Precipitation of platinum from sulfate solutions by barium chlorid, p. 72.) Pt.  
Edin. Phil. J. 1 (1819), 63; Ann. chim. phys. 14 (1820), 376; J. de Phys. 87 (1818), 462.
- 1819: 2. L. W. GILBERT. Das Newman'sche Gebläse mit verdichtetem Knallgas, nach seinen neuesten Verbesserungen durch Dr. E. D. Clarke. (Melts platinum, p. 265; alloy of platinum with 10 per cent gold described, p. 269.) Pt.  
Ann. der Phys. (Gilbert), 62 (1819), 247.
- 1819: 3. E. D. CLARKE. The gas blow-pipe, or art of burning the gaseous constituents of water. London, 1819. Pt.
- 1819: 4. E. D. CLARKE. On the alloy of platinum and lead. Pt.  
Ann. of Phil. (Thomson), 14 (1819), 229; Polyt. J. (Dingl.), 5 (1821), 125.
- 1819: 5. E. D. CLARKE. On the alloy of platinum and tin. Pt.  
Ann. of Phil. (Thomson), 14 (1819), 470.
- 1819: 6. R. W. FOX. Alloys of platinum (with tin, antimony and zinc). Pt.  
Ann. of Phil. (Thomson), 13 (1819), 467; Phil. Mag. 54 (1819), 72; Ann. Gén. Sci. Phys. (Brux.), 1 (1819), 363.
- 1819: 7. T. HOWSE. Query respecting the method of coating metals with platinum. Pt.  
Ann. of Phil. (Thomson), 14 (1819), 469.
- 1819: 8. L. W. GILBERT. Das Lämpchen ohne Flamme. Pt.  
Ann. der Phys. (Gilbert), 62 (1819), 337.
- 1819: 9. P. L. DULONG and A. T. PETIT. Recherches sur quelques points importants de la théorie de la chaleur. (Specific and atomic heat of platinum, p. 403.) Pt.  
Ann. chim. phys. 10 (1819), 395; Ann. der Phys. (Pogg.), 6 (1826), 394; J. für Chem. (Schweigger), 28 (1820), 122; Brugnatelli, Giornale, 2 (1819), 305; J. de Phys. 89 (1819), 80; Bul. Soc. Philom. Paris, 1819, 103; Phil. Mag. 54 (1819), 267; Ann. of Phil. (Thomson), 14 (1819), 189.

- 1820: 1. E. DAVY. On some combinations of platinum. (Platinum sulfate on alcohol, and as a test for gelatine; a grey oxid of platinum; platinum fulminate.) Pt.  
Phil. Trans. London, 110 (1820), 108; Proc. Roy. Soc. London, 2 (1833), 124; Ann. of Phil. (Thomson), 15 (1820), 297; 16 (1820), 385; J. für Chem. (Schweigger), 31 (1821), 340; Berzelius Jsb. 1 (1822), 59; Bul. Soc. Philom. Paris, 1820, 54; Phil. Mag. 56 (1820), 330; Ann. des Mines, 6 (1821), 148.
- 1820: 2. T. THOMSON. On arsenic. (Action of sodium arseniate on iridium, rhodium and platinum salts.) Pt, Ir, Rh.  
Ann. of Phil. (Thomson), 15 (1820), 84; J. für Chem. (Schweigger), 29 (1820), 435.
- 1820: 3. T. THOMSON. Repetition of Fox and Clarke's experiments on the alloy of platinum and tin. Pt.  
Ann. of Phil. (Thomson), 16 (1820), 18.
- 1820: 4. H. ROSE. Beiträge zur chemischen Kenntniss des Glimmers. (Oxydation des Platins durch Braunstein.) Pt.  
J. für Chem. (Schweigger), 29 (1820), 282.
- 1820: 5. G. B. SOWERBY. Crystallization of platinum. Pt.  
Ann. of Phil. 16 (1820), 233; Ann. chim. phys. 15 (1820), 111; Polytechn. J. (Dingl.), 3 (1820), 125.
- 1820: 6. R. HARE. Strictures on a publication entitled Clark's "Gas Blow-pipe." Pt.  
Amer. J. of Sci, 2 (1820), 281.
- 1820: 7. J. STODART and M. FARADAY. Experiments on the alloys of steel, made with a view to its improvement. Pt, Pd, Ir, Rh, Os.  
Quart. J. Sci. 9 (1820), 319; Ann. der Phys. (Gilbert), 66 (1820), 197; Ann. chim. phys. 15 (1820), 157; Ann. des Mines, 6 (1821), 261; Jern. Kont. Ann. 5 (1821), 120; J. de Phys. 91 (1820), 378; Phil. Mag. 56 (1820), 26; Edin. Phil. J. 3 (1820), 308; Arch. ges. Naturl. 2 (1824), 36.
- 1821: 1. ———. Extraordinary mass of platina discovered in Peru. Pt.  
Edin. Phil. J. 4 (1821), 214; Amer. J. of Sci. 4 (1822), 28.
- 1821: 2. J. J. BERZELIUS. Sur la composition des oxides du platine et de l'or. Pt.  
Ann. chim. phys. 18 (1821), 146; J. für Chem. (Schweigger), 33 (1821), 422; 34 (1822), 81; Quart. J. Sci. 12 (1822), 412; Edin. Phil. J. 6 (1822), 9; Ann. des Mines, 7 (1822), 137.
- 1821: 3. J. J. BERZELIUS. Om de svafvelbundna alkaliernas sammanfattning. (Sulfids of platinum and rhodium.) Pt, Rh.  
Akad. Handl. (Stockholm), 1821, i, 80; Ann. chim. phys. 20 (1822), 34, 113, 225; Quart. J. Sci. 11 (1821), 388; 14 (1822), 209; J. für

Chem. (Schweigger), 34 (1822), 22, 57; Ann. of Phil. (Thomson), 4 (1822), 284, 343.

- 1821: 4. J. B. BOUSSINGAULT. Sur la combinaison du silicium avec le platine. (Not compound of platinum and carbon as first thought.) Pt.

Ann. chim. phys. 16 (1821), 5; J. für Chem. (Schweigger) 32 (1821), 483; Phil. Mag. 59 (1822), 185; Berzelius Jsb. 2 (1823), 88; Archiv f. Bergbau (Karsten), 5 (1822), 158; Ann. des Mines, 7 (1822), 139.

- 1821: 5. T. THOMSON. (Oxid of platinum.) Pt.

Ann. chim. phys. 18 (1821), 146; Berzelius Jsb. 2 (1823), 87.

- 1821: 6. C. H. PFAFF. Ueber die Weinsteinsäure und das salzsaure Platin als Reagentien für Kali. Pt.

J. für Chem. (Schweigger), 33 (1821), 473.

- 1821: 7. J. MURRAY. On the change of colour in blue vegetable colours by metallic salts. (Colored green by platinic chlorid.) Pt.

Phil. Mag. 58 (1821), 273; J. für Chem. (Schweigger), 33 (1821), 486.

- 1821: 8. J. F. DANIELL. On a new pyrometer. (Platinum amalgam, p. 319.) Pt.

Quart. J. Sci. 11 (1821), 309; J. für Chem. (Schweigger), 33 (1821), 110.

- 1821: 9. J. MURRAY. On the alloys of platinum. Pt.

Edin. Phil. J. 4 (1821), 202.

- 1821: 10. T. J. SEEBECK. Magnetische Polarisation der Metalle und Erze durch Temperature-Differenz. (Platina tiegeln auf ihre chemische Reinheit durch Thermomagnetismus zu prüfen.) Pt.

Abhandl. Acad. Berlin. 1822-23, 265; J. für Chem. (Schweigger), 46 (1826), 101; J. techn. Chem. 2 (1828), 102; Ann. der Phys. (Pogg.), 6 (1826), 1, 114, 265.

- 1821: 11. J. P. CHARLTON. On the production of colours by mechanical division. (Effect of platinum black.) Pt.

Ann. of Phil. (Thomson), 18 (1821), 182; J. für Chem. (Schweigger), 33 (1821), 240.

- 1821: 12. J. P. CHARLTON. On the black enamel obtained from platina. (Colors from platinum and iridium.) Pt, Ir.

Ann. of Phil. (Thomson), 18 (1821), 337; J. für Chem. (Schweigger), 34 (1822), 253; Polyt. J. (Dingl.), 7 (1822), 350.

- 1821: 13. E. D. CLARKE. Observations upon the gas blow-pipe. (Reduction of the platinum metals.) Pt, Pd, Ir, Rh, Os.

Ann. of Phil. (Thomson), 17 (1821), 424.



- 1822: 1. E. BARRUEL. Process for procuring pure platinum, palladium, rhodium, iridium and osmium from the ores of platinum.  
Pt, Pd, Ir, Rh, Os.  
Quart. J. Sci. 12 (1822), 246; Phil. Mag. 59 (1822), 171 (in full);  
Polyt. J. (Dingl.), 8 (1822), 231; Berzelius Jsb. 3 (1824), 105.
- 1822: 2. L. GMELIN and F. WÖHLER. Neue Cyanverbindungen. (Potassium platino- and pallado-cyanids.) Pt, Pd.  
Gmelin's Handbuch der theoret. Chemie, 3te Auflage, 2, ii, 1692;  
J. für Chem. (Schweigger), 36 (1822), 230.
- 1822: 3. J. MURRAY. On the combination of the earths with platinum.  
(With antimony, zirconium, glucinum, aluminum, potassium.) Pt.  
Edin. Phil. J. 6 (1822), 385.
- 1822: 4. J. STODART and M. FARADAY. On the alloys of steel. (With the platinum metals.) Pt, Pd, Ir, Rh, Os.  
Phil. Trans. London, 112 (1822), 253; Proc. Roy. Soc. London, 2  
(1833), 169; Ann. chim. phys. 21 (1822), 62; Edin. Phil. J. 7  
(1822), 350; Ann. of Phil. (Thomson), 21 (1823), 202; Ann. der  
Phys. (Gilbert), 72 (1822), 225; Mag. f. Naturvid. 2 (1823), 216;  
Phil. Mag. 60 (1822), 363.
- 1822: 5. ————. Email noir obtenu avec le platine. Pt.  
Ann. chim. phys. 20 (1822), 198; Polyt. J. (Dingl.), 8 (1822), 506.
- 1822: 6. J. W. DÖBEREINER. Glühendes Verbrennen des Alkohols  
durch erhitzte Metalle und Metalloxyde. (Durch Platindraht.) Pt.  
J. für Chem. 34 (1822), 91.
- 1822: 7. ————. Sur l'acide formé par la combustion de l'éther  
au moyen d'un fil de platine. Pt.  
Ann. chim. phys. 20 (1822), 223.
- 1823: 1. C. C. On the existence of chrome in the ore of platinum.  
Ann. of Phil. (Thomson), 22 (1823), 198. Pt.
- 1823: 2. PUYMAURIN. Note sur le palladium. (Note on palladium,  
prices, &c.) Pd.  
Bul. Soc. Encour. (Paris), 22 (1823), 163; Bibl. Univ. 83 (1823),  
235; Polyt. J. (Dingler), 12 (1823), 375; J. für Chem. (Schweigger),  
39 (1823), 356.
- 1823: 3. B. SILLIMAN. Test for platinum. (Hydriodic acid.) Pt.  
Amer. J. of Sc. 6 (1823), 276; J. für Chem. (Schweigger), 42 (1824),  
121; Polyt. J. (Dingl.), 12 (1823), 465; Ann. of Phil. (Thomson),  
22 (1823), 397; Ann. des Mines, 10 (1825), 176; Mag. für Pharm.  
5 (1824), 262.

- 1823: 4. J. J. BERZELIUS. Undersökning af fluss-spatssyran och dess märkvärdigaste föreningar. (Flussspathsaures Platinoxid, Ann. der Phys. (Pogg.), 1 : 36, 47; Flussspathsaures Kieselplatinoxid, 1 : 201; Einwirkung von Silicium auf Platin und Rhodium, 1 : 220.) Pt, Rh.  
Acad. Handl. Stockholm, 1823, 284; Ann. der Phys. (Pogg.), 1 (1824), 36, 47, 201, 220; Ann. chim. phys. 27 (1824), 53, 167; Quart. J. Sci. 18 (1825), 156; Ann. of Phil. (Thomson), 24 (1824), 337, 450.
- 1823: 5. R. BRANDES. Monographie der Kamphersäure. (Kamphersaures Platinoxid, p. 299.) Pt.  
J. für Chem. (Schweigger), 38 (1823), 269.
- 1823: 6. J. W. DÖBEREINER. Neuentdeckte merkwürdige Eigenschaften des Platin-suboxyds, des oxydirten Schwefel-Platins, und des metallischen Platinstaubes. (Oxydation of alcohol to acetic acid.) Pt.  
J. für Chem. (Schweigger), 38 (1823), 321; Ann. chim. phys. 24 (1823), 91 (in full); Bibl. Brit. [2], 24 (1823), 54; Edin. Phil. J. 10 (1824), 153; Ann. der Phys. (Gilbert), 74 (1823), 269; Quart. J. Sci. 16 (1823), 375; Ann. of Phil. 22 (1823), 464; Phil. Mag. 62 (1823), 289, 396; Amer. J. of Sci. 7 (1824), 387; N. J. der Pharm. (Trommsd.), 7 (1823), 119; Ann. des Mines, 9 (1824), 243; Mag. für Pharm. 4 (1823), 49, 127.
- 1823: 7. J. W. DÖBEREINER. Platin und Wasserstoffgas. Pt.  
Oken, Isis, 1823, 989.
- 1823: 8. J. W. DÖBEREINER. Ueber das Entglühen des Platinpulvers. Pt.  
J. für Chem. (Schweigger), 39 (1823), 159.
- 1823: 9. P. L. DULONG and L. J. THENARD. Note sur la propriété qui possèdent quelques métaux de faciliter la combinaison des fluides élastiques. Pt, Pd, Ir.  
Ann. chim. phys. 23 (1823), 440; Ann. der Phys. (Gilbert), 76 (1824), 83; Bibl. Brit. [2], 24 (1823), 195; Froriep, Notizen, 6 (1824), 83; Mém. Acad. Sci. Paris. 5 (1821), 476; Quart. J. Sci. 17 (1824), 138; J. für Chem. (Schweigger), 39 (1823), 205; Phil. Mag. 62 (1823), 282; Ann. of Phil. (Thomson), 6 (1823), 376; Mag. für Pharm. 5 (1824), 142.
- 1823: 10. P. L. DULONG and L. J. THENARD. Nouvelles observations sur la propriété dont jouissent certains corps de favoriser la combinaison des fluides élastiques. Pt.  
Ann. chim. phys. 24 (1823), 380; Ann. der Phys. (Gilbert), 76 (1824), 89; Mém. Acad. Sci. Paris. 5 (1821), 481; J. für Chem. (Schweigger), 40 (1824), 229; Moniteur (1823), Nov. 12; Arch. ges. Naturl. 1 (1824), 81; Mag. für Pharm. 8 (1824), 244.

- 1823: 11. A. GARDEN. On the ignition of platina by hydrogen gas.  
Pt, Ir.  
Ann. of Phil. (Thomson), 22 (1823), 466; J. für Chem. (Schweigger), 40 (1823), 115.
- 1823: 12. C. G. GMELIN. Ueber Döbereiner's Entdeckung der Eigenschaft des Platinstaubes, Wasserstoff zu entzünden. Pt.  
J. für Chem. (Schweigger), 38 (1823), 515; Bibl. Brit. [2], 24 (1823), 278.
- 1823: 13. L. W. GILBERT, CHLADNI and J. F. DANIELL. Ueber das Glühlämpchen. Pt.  
Ann. der Phys. (Gilbert), 75 (1823), 95.
- 1823: 14. W. HERAPATH. On Döbereiner's new experiment with hydrogen gas and platinum in a finely divided state. (Read before Bristol Phil. Soc. of Inquirers.) Pt.  
Phil. Mag. 62 (1823), 286; J. für Chem. (Schweigger), 39 (1823), 255; Mag. für Pharm. 5 (1824), 143, 240.
- 1823: 15. K. KARMARSH. Ueber das Glühen von Metalldrähten in den Dämpfen flüchtiger Substanzen. Pt.  
Ann. der Phys. (Gilbert), 75 (1823), 83.
- 1823: 16. C. H. PFAFF. Ueber die von Döbereiner entdeckte merkwürdige Eigenschaft des metallischen Platinastaubes oder Platinschwammes. Pt.  
J. für Chem. (Schweigger), 40 (1823), 1; Mag. für Pharm. 6 (1824), 138; 8 (1824), 243.
- 1823: 17. A. PLEISCHL. Beobachtungen über das Entglühen des Platinpulvers im Hydrogenstrome. Pt.  
J. für Chem. (Schweigger), 39 (1823), 142, 201; Bibl. Brit. [2], 25 (1824), 112; 26 (1824), 38; J. d. l'Inst. roy. No. 32.
- 1823: 18. A. PLEISCHL. Beobachtungen über das Entglühen des Palladiums im Hydrogenstrome. Pd.  
J. für Chem. (Schweigger), 39 (1823), 351; Ann. der Phys. (Gilbert), 76 (1824), 98.
- 1823: 19. J. S. C. SCHWEIGGER. Ueber Döbereiner's neues Feuerprincip. Pt.  
J. für Chem. (Schweigger), 39 (1823), 205; 40 (1824), 10, 239, 277; 41 (1824), 402; Phil. Mag. 64 (1824), 3.
- 1823: 20: J. R. BRÉANT. Description d'un procédé à l'aide duquel on obtient une espèce d'acier fondu semblable à celui des lames damassées orientales. (Palladium steel.) Pd.  
Ann. chim. phys. 24 (1823), 388; Bibl. Univ. 83 (1823), 236; Edinb. Phil. J. 9 (1823), 404; Ann. des Mines, 9 (1824), 319; Ann. of

Phil. (Thomson), 8 (1824), 267; Arch. ges. Naturl. 2 (1824), 38; J. für Chem. (Schweigger), 40 (1824), 295; Quart. J. Sci. 18 (1825), 386; Techn. Rep. (Gill), 6 (1824), 49; Mag. für Pharm. 4 (1823), 215.

- 1823: 21. J. R. BRÉANT. (Palladium medals.) Pd.  
Moniteur (1823), June 22; Arch. ges. Naturl. 2 (1824), 244.
- 1823: 22. A. C. BECQUEREL. Sur les fils très-fins de platine et d'acier. Pt.  
(Working of platinum.)  
Ann. chim. phys. 22 (1823), 113; J. für Chem. (Schweigger), 39 (1823), 374; Mém. de l'Inst. Paris, 11 (1832), 13.
- 1823: 23. A. C. BECQUEREL. Du développement de l'électricité par le contact de deux portions d'un même métal, dans un état suffisamment inégal de temperature. Pt.  
Ann. chim. phys. 23 (1823), 135; J. für Chem. (Schweigger), 39 (1823), 448; 44 (1825), 176.
- 1824: 1. LE BAILLIF. (Mittel das Palladium von der Platina zu unterscheiden.) (By iodine and cuprous chloride.) Pt, Pd.  
Ann. de l'Industrie Nation. 15 (1824); J. für Chem. (Schweigger), 42 (1824), 120; Polyt. J. (Dingl.), 13 (1824), 275; Berzelius Jsb. 5 (1826), 142.
- 1824: 2. A. M. DEL RIO. Analyse d'un alliage d'or avec du rhodium, de la Maison du Départ (Apatado) de Mexico. Rh.  
Sol, Dec. 11, 1824; Ann. chim. phys. 29 (1825), 137; Amer. J. of Sci. 11 (1826), 298; J. für Chem. (Schweigger), 47 (1826), 65; Ann. der Phys. (Pogg.), 10 (1827), 322; Arch. für Bergbau (Karsten), 11 (1826), 386; Ann. of Phil. (Thomson), 10 (1825), 251; Ann. des Mines, 12 (1826), 323.
- 1824: 3. A. ADIE. Hydro-pneumatic lamp. Description of lamp devised by Mr. Adie as an improvement on Garden's lamp. Pt.  
Edin. J. Sci. 1 (1824), 144; Ann. der Phys. (Pogg.), 2 (1824), 333.
- 1824: 4. S. F. DANA. Ignition of platinum (by vapor of alcohol or ether). Pt.  
Amer. J. of Sci. 8 (1824), 198; J. für Chem. 43 (1825), 380.
- 1824: 5. J. W. DÖBEREINER. Ueber Wasserbildung, und über den Einfluss der Platina auf Hydrogen. Pt.  
J. für Chem. (Schweigger), 42 (1824), 60; Ann. of Phil. (Thomson), 25 (1825), 213; Phil. Mag. 65 (1825), 150.
- 1824: 6. J. W. DÖBEREINER. Das Platin, etc., als Begünstiger der Gasverbindung. Pt.  
Archiv ges. Naturl. 2 (1824), 225.

- 1824: 7. J. W. DÖBEREINER. Ueber Wasserbildung, und über den Einfluss der Platina auf Hydrogen. Pt.  
J. für Chem. (Schweigger), 42 (1824), 60; Phil. Mag. 65 (1825), 150.
- 1824: 8. A. FYFE. Description of a hydro-pneumatic lamp. Pt.  
Edin. Phil. J. 11 (1824), 341; Ann. der Phys. (Pogg.), 2 (1824), 329; Polyt. J. (Dingl.), 15 (1824), 420; Bibl. Brit. [2], 28 (1825), 196.
- 1824: 9. L. W. GILBERT. Noch einiges von Herrn Döbereiner aus England. (Glühlämpchen.) Pt.  
Ann. der Phys. (Gilbert), 76 (1824), 102.
- 1824: 10. W. HENRY. On the action of finely divided platinum on gaseous mixtures, and its application to their analysis. Pt.  
Phil. Trans. London. 14 (1824), 266; Proc. Roy. Soc. London, 2 (1833), 216; Amer. J. of Sci. 12 (1827), 181; Ann. of Phil. (Thomson), 25 (1825), 416; Phil. Mag. 65 (1825), 269; Ann. des Mines [2], 1 (1827), 172; Berzelius Jsb. 6 (1827), 147.
- 1824: 11. K. W. G. KASTNER. Ueber die Imponderabilien, Magnetismus, Elektrizität, Licht und Wärme, etc. (Platinum sponge and hydrogen.) Pt.  
Arch. ges. Naturl. 1 (1824), 68; 2 (1824), 230.
- 1824: 12. G. OSANN. Das Platin, etc., als Begünstiger der Gasverbindungen. Pt.  
Arch. ges. Naturl. 2 (1824), 448.
- 1824: 13. P. W. SCHMIDT. Ueber die Zündapparate nach Döbereiner. Pt.  
J. für Chem. (Schweigger), 42 (1824), 247.
- 1824: 14. E. TURNER. Experiments on the application of Professor Döbereiner's recent discovery to eudiometry. (Read before Roy. Soc. Edin.) Pt.  
Edin. Phil. J. 11 (1824), 99; Ann. der Phys. (Pogg.), 2 (1824), 210.
- 1824: 15. ———. Repetition of Döbereiner's experiments by Children, and Daniel and Turner. Pt.  
Edin. Phil. J. 21 (1824), 99; J. für Chem. (Schweigger), 43 (1824), 380 ("from J. of Sci. 32, 374").
- 1824: 16. J. W. DÖBEREINER. Ueber das leichtflüssige Metall und eine kaltmachende Metallmischung. (Wärme-entwicklung wenn Platin und Zink-Natrium auf einander wirken.) Pt.  
J. für Chem. (Schweigger), 42 (1824), 182; Arch. ges. Naturl. 3 (1824), 89; Quart. J. Sci. 19 (1825), 341.

- 1824: 17. F. P. DULK. Bemerkungen über Elektromagnetismus. (Conductivity of platinum, p. 35; Action on needle, p. 38. From "Ueber Magnetismus," &c., Königsberg, 1824). Pt.  
Arch. ges. Naturl. 1 (1824), 32.
- 1825: 1. A. VON HUMBOLDT. Vorkommen der Platina und des Palladiums in Brasilien. Pt, Pd.  
J. für Chem. (Schweigger), 45 (1825), 54.
- 1825: 2. A. LAUGIER. Examen du platine trouvé en Russie. Pt.  
Ann. chim. phys. 29 (1825), 289; J. für Chem. (Schweigger), 46 (1826), 94; Phil. Mag. 66 (1825), 285; Berzelius Jsb. 6 (1827), 212; Ann. des Mines, 12 (1826), 324.
- 1825: 3. A. LAUGIER. Examen du platine trouvé en Sibérie. Pt.  
Ann. sci. nat. 5 (1825), 333.
- 1825: 4. W. C. ZEISE. En ny Forbindelse af Platinets Forchlorid behandlet med Viinaand. (Compound of platinum chlorid with carbon monoxid.) Pt.  
Afh. Danske Vid. Selsk. 3 (1828), 45; Overs. Danske Vid. Selsk. 1825-26, 13; Berzelius Jsb. 7 (1828), 131; Ann. der Phys. (Pogg.), 9 (1827), 632; Mag. für Pharm. 20 (1827), 346.
- 1825: 6. J. J. BERZELIUS. Om Svafvelsalter. (Compounds of platinum sulfid with sulfids of carbon, arsenic, molybdenum, tungsten and tellurium.) Pt.  
Kong. Vet. Acad. Handl. 1825, 232; 1826, 53; Ann. der Phys. (Pogg.), 6 (1826), 453; 7 (1826), 150, 277; 8 (1826), 282, 419; Ann. chim. phys. 32 (1826), 60, 166, 265, 393; Brugnatelli, Giorn. 9 (1826), 297, 435.
- 1825: 7. A. PLEISCHL. Ueber Hydrojodsäure als Reagens für Platin. Pt.  
Arch. ges. Naturl. 5 (1825), 160; J. für Chem. (Schweigger), 43 (1825), 385; Ann. des Mines [2], 1 (1827), 173.
- 1825: 8. A. PLEISCHL. Ueber die jodige Säure. (Reactions with platinum and palladium.) Pt, Pd.  
J. für Chem. (Schweigger), 45 (1825), 1; Arch. ges. Naturl. 6 (1825), 155.
- 1825: 9. G. BISCHOF. Oxydation des Platins durch Schmelzen des Aetzkalis. Pt.  
J. für Chem. (Schweigger), 45 (1825), 209.
- 1825: 10. C. G. GMELIN. Ueber die Wirkung des . . . Osmiums, Platins, Iridiums, Rhodiums, Palladiums . . . auf den thierischen Organismus. Os, Pt, Ir, Rh, Pd.  
J. für Chem. (Schweigger), 43 (1825), 110; J. chim. méd. 2 (1826), 188; 3 (1827), 126, 388; Edinb. J. Med. Sci. 3 (1827), 324.

- 1825: 11. T. GILL. On a suggestion for improving Dr. Fyfe's Döbereiner's lamp. Pt.  
Techn. Repository, 6 (1825), 297; Polyt. J. (Dingl.), 16 (1825), 301.
- 1825: 12. G. BISCHOF. Der . . . Döbereiner'sche Versuch, ein ziemlich empfindliches Reagens auf Platin. Pt.  
J. für Chem. (Schweigger), 45 (1825), 212.
- 1825: 13. H. DAVY. On the safety lamp for coal miners, with some researches on flame. (Aphlogistic lamp.) Pt.  
2nd ed. with additions; Ann. of Phil. (Thomson), 25 (1825), 459.
- 1825: 14. H. A. VON VOGEL. Ueber eine Feuererscheinung des braunen Bleioxyds bei Berührung mit schweflichtsaurem Gas. (Bemerkungen über das Döbereiner'sche Feuerzeug, &c.) Pt.  
Arch. ges. Naturl. 4 (1825), 434.
- 1825: 15. J. F. JOHN. Ueber Döbereiner'sche Platinfeuerzeuge. Pt.  
Arch. ges. Naturl. 4 (1825), 491.
- 1825: 16. F. P. DULK. Etwas über das Döbereiner'sche Phänomen. Pt.  
Arch. ges. Naturl. 6 (1825), 467.
- 1825: 17. ———. (Agency of platinum in effecting formation of water.) Pt.  
"Bull. des Sci. No. 12"; Phil. Mag. 65 (1825), 158.
- 1825: 18. S. STRATINGH. Platine spongieux et camphre. Pt.  
J. de Pharm. 11 (1825), 195.
- 1825: 19. F. WÖHLER. Ueber die Wirkung des Palladiums auf die Weingeist Flamme. Pd.  
Ann. der Phys. (Pogg.), 3 (1825), 71; Berzelius Jsb. 5 (1825), 143; Mag. für Pharm. 12 (1825), 282.
- 1825: 20. ———. Discussions on disputed inventions. 2. Daniell's platina pyrometer, partly anticipated by Mr. Guyton. Pt.  
Edin. J. of Sci. 2 (1825), 147.
- 1825: 21. ———. Mr. Nicholas Mill's platina pyrometer. Pt.  
Edin. J. of Sci. 2 (1825), 338.
- 1825: 22. ———. (Platina strings for musical instruments.) Pt.  
Neues Kunst und Gewerbeblatt. (Apr. 1825); Edin. Phil. J. 14 (1826), 200. (Also Musical Gazette, Leipzig.)
- 1826: 1. A. VON HUMBOLDT (J. B. Boussingault). Ueber die Provinz Antioquia und die neu entdeckte Lagerstätte der Platina auf Gängen. (Also platinum in the Oural mountains.) (Letter from Boussingault, Ann. der Phys. (Pogg.), 7 : 520.) Pt, Pd, Ir, Os, Rh.  
Hertha, 7 (1826), 263; Quart. J. of Sci. 22 (1826), 225; J. de Pharm. 12 (1826), 434; Ann. chim. phys. 32 (1826), 204; Ann. der Phys.

(Pogg.), 7 (1826), 515; J. chim. méd. 2 (1826), 397; Edin. J. of Sci. 5 (1826), 323; Amer. J. of Sci. 12 (1827), 384; J. für Chem. (Schweigger), 47 (1826), 368; Phil. Mag. 68 (1826), 306; Bul. Univ. Nov. (1826); Le Globe, Jy. 20 (1826); Edin. N. Phil. J. 2 (1827), 197; Ann. des Mines [2], 1 (1827), 175, 178; Berzelius Jsb. 7 (1828), 184; Mag. für Pharm. 16 (1826), 101, 353; Ztsch. für Min. 1826, No. 12.

- 1826: 2. ———. Platina found in Russia. Pt.  
Edin. Phil. J. 14 (1826), 173.
- 1826: 3. J. MENGE. Geognostische Nachrichten aus Sibirien; Bemerkungen über die Gold- und Platina-Bergwerke des Ural-Gebirges. Pt.  
Leonhard, Ztsch. für Min. 2 (1826), 245, 508; Ann. Sci. Nat. 10 (1827), 386; Edinb. N. Phil. J. 2 (1827), 199.
- 1826: 4. A. BREITHAUP. Mineralogische Untersuchung des russischen Platinsandes. Pt, Pd, Ir, Os, Rh.  
Ann. der Phys. (Pogg.), 8 (1826), 500; Phil. Mag. [2], 3 (1828), 72; Edinb. N. Phil. J. 3 (1827), 272; Mag. für Pharm. 20 (1827), 210; Berzelius Jsb. 7 (1828), 185; Ann. chim. phys. 38 (1828), 443; J. des Mines russes, Aug. (1827); Ann. des Mines [2], 3 (1828), 283.
- 1826: 5. G. OSANN. Untersuchung der russischen Platina. (Very full study of the ore; contains announcement of three new metals, ruthenium, pluran, and polin, 13:287. Pluran was perhaps ruthenium, but Osann's ruthenium and polin were errors. Claus.) Pt, Pd, Ir, Os, Rh, [Ru, Po, Plu].  
Ann. der Phys. (Pogg.), 8 (1826), 505; 11 (1827), 311; 13 (1828), 283; 14 (1828), 329; Arch. ges. Naturl. 16 (1829), 129; Edinb. New Phil. J. 3 (1827), 276; Quart. J. of Sci. 26 (1828), 438; Phil. Mag. [2], 2 (1827), 391; Heusman Repert. de Chim. Sept. (1827); J. chim. méd. 4 (1828), 554; Bull. math. chim. (Férussac), Sept. (1828); Mag. für Pharm. 20 (1827), 346; 24 (1828), 185; Amer. J. of Sci. 16 (1829), 384; Berzelius Jsb. 7 (1828), 185; 8 (1829), 206.
- 1826: 6. T. THOMSON. Analysis of the ore of iridium. (Attempt to determine atomic weights.) Ir, Rh.  
Ann. of Phil. (Thomson), 2 (1826), 17; Mag. für Pharm. 16 (1826), 353; J. für Chem. (Schweigger), 47 (1826), 55; Polyt. J. (Dingl.), 16 (1826), 111; Ann. des Mines, 12 (1826), 326; Berzelius Jsb. 7 (1828), 183.
- 1826: 7. A. J. BALARD. Mémoire sur une substance particulièrement contenue dans l'eau de la mer (le brôme). (Compound of platinum and bromin, p. 362.) Pt.  
Ann. chim. phys. 32 (1826), 337; Ann. der Phys. (Pogg.), 8 (1826), 333; J. für Chem. (Schweigger), 48 (1826), 87; Ann. of Phil.



(Thomson), 28 (1826), 416; J. de Pharm. 12 (1826), 517; N. J. der Pharm. (Trommsd.), 14 (1827), 80.

- 1826: 8. G. FORCHHAMMER. Bemaerkninger over et nyt chemisk Prøvemiddel paa Platin, det salpetersure Quiksølvforilte. (HgNO<sub>3</sub>.) Pt.  
Overs. Danske Vid. Selsk. 1826-27, 8; J. für Chem. (Schweigger), 52 (1828), 3; Mag. für Pharm. 24 (1828), 393.
- 1826: 9. H. B. MILLER. On the oxidation of palladium during its effecting the union of the hydrogen and oxygen gases from ether, alcohol, etc. Pd.  
Ann. of Phil. (Thomson), 28 (1826), 20.
- 1826: 10. J. W. DÖBEREINER. Neue Bereitung des Platinsuboxyds, höchst dünner Platinüberzug statt Platinschwamm; Gebrauch des Essiglämpchens und Bereitung der Essigsäure im Grossen mitelst des Platinsuboxyds. Pt.  
Arch. ges. Naturl. 9 (1826), 341; Mag. für Pharm. 18 (1827), 342.
- 1826: 11. ————. Observations on alloys or mixtures of metals. (Alloys of platinum metals with copper, molybdenum, bismuth, gold, tin, iron, and arsenic are mentioned.) Pt, Pd, Rh, Ir.  
Franklin Jour. 1 (1826), 316; from Dictionnaire Technologique; from Thénard, Chimie Élémentaire.
- 1826: 12. W. NASSE. Versuche mit einigen Metallen . . . in Porzellanfeuer. (Unschmelzbarkeit des Platins.) Pt.  
J. für Chem. (Schweigger), 46 (1826), 80.
- 1826: 13. J. W. DÖBEREINER. Platinschwammbereitung und Gebrauch. Pt.  
J. für Chem. (Schweigger), 47 (1826), 119; Phil. Mag. [2], 2 (1827), 388; Heusman Rep. de Chim.; Berzelius Jsb. 7 (1828), 130.
- 1826: 14. H. B. MILLER. Addition to the list of substances that cause a coil of platinum wire to continue in a state of incandescence, etc. Pt.  
Ann. of Phil. (Thomson), 28 (1826), 21.
- 1826: 15. J. J. BERZELIUS. Ueber die Bestimmung der relativen Anzahl von einfachen Atomen in chemischen Verbindungen. Pt, Pd, Ir, Rh, Os.  
Ann. der Phys. (Pogg.), 8 (1826), 178.
- 1826: 16. S. MARIANINI. Expériences pour déterminer la force électromotrice relative des conducteurs de la même classe. Pt.  
Ann. chim. phys. 33 (1826), 14; from Saggio di esperienze elettromotriche &c. Venezia, 1825; J. für Chem. (Schweigger), 47 (1827), 47.

- 1827: 1. N. MAMYSCHIEFF. Beschreibung der Entdeckung der Platina in Sibirien. Pt.  
Ztsch. für Min. (Leonhard), 1827, 265; Berzelius Jsb. 8 (1829), 202.
- 1827: 2. A. T. KUPFFER. Ueber das Vorkommen des Platins in Sibirien. Pt.  
Arch. ges. Naturl. 12 (1827), 236.
- 1827: 3. ————. Sur le minéral de platine de Sibérie. Pt.  
J. des Mines russ. Aug. (1827); Ann. des Mines [2], 3 (1828), 284.
- 1827: 4. ————. (Platinum mines of the Ural mts.) Pt.  
Bul. Univ. Sept. 1827; Amer. J. of Sci. 14 (1828), 204.
- 1827: 5. A. VON HUMBOLDT. Grösse der Körner von gediegenem Platin. Pt.  
Ann. der Phys. (Pogg.), 10 (1827), 487; Ann. chim. phys. 37 (1828), 222; Amer. J. of Sci. 16 (1829), 389; Bull. math. chim. (Férussac), Nov. (1828); Berzelius Jsb. 8 (1829), 203; Mag. für Pharm. 28 (1829), 129.
- 1827: 6. ARKHIPOFF. Nouveau moyen d'extraire l'or du minéral de platine. Pt.  
J. des Mines russ. ; Ann. des Mines [2], 1 (1827), 174.
- 1827: 7. ————. Tafel der Atomengewichte der einfachen Körper und deren Oxyde. (Atomic weights.) Pt, Pd, Rh.  
Ann. der Phys. (Pogg.), 10 (1827), 340.
- 1827: 8. G. OSANN. Merkwürdiges Verhältniss des Eigengewichts pulverisirter Körper zu ihren Atomengewichten. Pt.  
Arch. ges. Naturl. 12 (1827), 487.
- 1827: 9. J. B. VAN MONS. Salzaures Platin. (Verflüchtigung eines weisses Precipitäs mit Chlorplatin.) Pt.  
Arch. ges. Naturl. 10 (1827), 59.
- 1827: 10. P. A. VON BONSDORFF. Extrait d'une lettre à M. Gay-Lussac. (Combination of chlorplatinic acid with copper, zinc, manganese, iron, etc., chlorids.) Pt.  
Ann. chim. phys. 34 (1827), 145; J. für Chem. (Schweigger), 49 (1827), 324.
- 1827: 11. ————. (Note on double chlorids of platinum and palladium.) Pt, Pd.  
Ann. der Phys. (Pogg.), 11 (1827), 124.
- 1827: 12. N. W. FISCHER. Zur Geschichte des Arseniks. (Rauchen des mit Platin überzogenen Arseniks nach Erhitzen, p. 228.) Pt.  
Arch. ges. Naturl. 11 (1827), 224.

- 1827: 12a. E. MITSCHERLICH. Ueber eine neue Oxydationsstufe des Selens. (Einwirkung der Selensäure auf Platin, p. 630.) Pt.  
Ann. der Phys. (Pogg.), 9 (1827), 623; Ann. chim. phys. 36 (1827), 100; Edinb. J. of Sci. 8 (1828), 294; Quart. J. of Sci. 2 (1827), 471.
- 1827: 13. N. W. FISCHER. Zur Geschichte des Palladiums. (Verhalten zu den Säuren, p. 192; zu Reagentien, 197; Doppelsalze, 200.) Pd.  
J. für Chem. (Schweigger), 51 (1827), 192; Phil. Mag. [2], 4 (1828), 230; Heusman Rep. de Chim. Feb. (1828); Ann. des Mines [2], 5 (1829), 168; Berzelius Jsb. 8 (1829), 183.
- 1827: 14. N. W. FISCHER. Beiträge zur Kenntniss der Erzmétalle. (Properties of platinum and palladium, p. 227.) Pt, Pd.  
Arch. ges. Naturl. 13 (1828), 223; from Bul. d. nat. wiss. Sect. d. Schlesischen Gesell. für Vaterländ. Cultur, 1827.
- 1827: 15. N. W. FISCHER. Metallreduction auf nassem Wege, durch andere Metalle. (Palladium, 9 : 256 and 10 : 607. Osmium, 12 : 499. Platinum, palladium and osmium, 12 : 504.) Pt, Pd, Os.  
Ann. der Phys. (Pogg.), 9 (1827), 256; 10 (1827), 607; 12 (1828), 499, 504; J. de Pharm. 16 (1830), 133.
- 1827: 16. M. J. EICHFELD. Eine Erfindung das Platin zu schmelzen. Pt.  
Journal d'Odessa, 1827, 63; Bul. d. Sci. tech. (1828), 280; J. techn. Chem. 2 (1828), 402; Polyt. J. (Dingler), 28 (1828), 477; J. Frank. Inst. [2], 2 (1828), 249; Berzelius Jsb. 9 (1830), 106.
- 1827: 17. K. W. G. KASTNER. Durchscheinbarkeit des Platins. Pt.  
Arch. ges. Naturl. 10 (1827), 490 (foot-note).
- 1827: 18. T. COOPER. Experiments and observations on some alloys of platinum. (Alloys; speculum metal containing platinum.) Pt.  
Franklin Journ. 3 (1827), 198; Techn. Repository, 1 (1827), 13; J. techn. Chem. 1 (1828), 350; Polyt. J. (Dingler), 25 (1827), 401.
- 1827: 19. ———. (Notes on alloys of gold, palladium and rhodium.) Pd, Rh.  
Ann. der Phys. (Pogg.), 10 (1827), 321.
- 1827: 20. [J. R.] BRÉANT. (Siphon of platinum.) Pt.  
J. de Pharm. June, 1827; J. für Chem. (Schweigger), 50 (1827), 383.
- 1827: 21. C. DESPRETZ. Sur la conductibilité des principaux métaux et de quelques substances terreuses. (Conductivity of platinum.) Pt.  
Ann. chim. phys. 36 (1827), 422; Ann. der Phys. (Pogg.), 12 (1828), 282; Quart. J. of Sci. 1 (1828), 220.

- 1827: 22. W. S. HARRIS. On the relative powers of various metallic substances as conductors of electricity. (Conductivity of platinum.) Pt.  
Phil. Trans. London, 107 (1827), 18; Proc. Roy. Soc. London, 2 (1833), 298; Ann. der Phys. (Pogg.), 12 (1828), 280; Bull. math. chim. (Férussac), 8 (1827), 33.
- 1828: 1. M. VON ENGELHARDT. Die Lagerstätte des Goldes und Platins im Ural-Gebirge. Riga, 1828. Pt, Pd, Ir, Os, Rh.  
Mag. für Pharm. 24 (1828), 193 (quite full); Arch. ges. Naturl. 21 (1831), 160.
- 1828: 2. F. H. Bemerkungen über die Lagerstätte des Platins am Ural. Pt.  
Ann. der Phys. (Pogg.), 13 (1828), 566.
- 1828: 3. ————. Native platinum from Nijne Taguiski. Pt.  
Monthly Mag. Feb. 1828; Phil. Mag. [2], 3 (1828), 232.
- 1828: 4. C. M. MARX UND ANDERE. Platinamassen von beträchtlichen Grösse und Reichthum an Platin und Gold im Ural. Pt.  
J. für Chem. (Schweigger), 54 (1828), 466.
- 1828: 5. ————. Largest known masses of native platina. Pt.  
Edin. N. Phil. J. 4 (1828), 185; Phil. Mag. [2], 4 (1828), 308.
- 1828: 6. A. BREITHAUPT. Die Krystallisation der Markase. (Iridosmin, p. 171.) Ir, Os.  
J. für Chem. (Schweigger), 52 (1828), 165.
- 1828: 7. A. BREITHAUPT. Notiz über Verkauf des russischen Platins. Pt.  
J. für Chem. (Schweigger), 52 (1828), 109; Phil. Mag. [2], 4 (1828), 458.
- 1828: 8. ————. Münzen aus Platina. (Note.) Pt.  
Mag. für Pharm. 23 (1828), 229; Ann. of Phil. (Thomson) (1828), Dec.; Edinb. N. Phil. J. 6 (1829), 197.
- 1828: 9. J. J. BERZELIUS. Försök öfver de metaller som åtfölja Platinan samt öfver sättet att analysera Platinans nativa legeringar eller Malmer. (Atomic weights, salts, oxalates, sulfates, etc.) (Considered ruthenium as iridium.) (Rhodium salts, p. 32; palladium salts, 46; iridium salts, 59; osmium salts, 81; separation of platinum from ore, 103; platinum sulfid, 114.) Pt, Pd, Ir, Os, Rh.  
Kong. Vet. Acad. Handl. (Stockholm), 1828, 25; Ann. chim. phys. 40 (1829), 51, 138, 257, 337; Ann. der Phys. (Pogg.), 13 (1828), 435, 527; J. techn. Chem. 3 (1828), 465; Phil. Mag. [2], 5 (1829), 395; 6, 146; Amer. J. of Sci. 18 (1830), 162; Polyt. J. (Dingler), 30 (1828), 315; Oken, Isis, 22 (1829), 279; Quart. J. of Sci. 2:

(1829), 174; *Ann. des Mines* [2], 5 (1829), 326; *Mag. für Pharm.* 26 (1829), 106, 279; *Berzelius Jsb.* 9 (1830), 114, 163, 169, 171, 180, 194; 10 (1831), 112.

- 1828: 10. P. A. VON BONSDORFF. Bidrag till afgörande af frågan om Chlor, Iod. m. fl. metalloider, i likhet med syre, äro syra- och basbildande Kroppar. (Chloroplatinates, and bromoplatinates and palladates.) Pt, Pd.

*Kong. Vet. Acad. Handl. Stockholm*, 1828, 174; 1830, 117; *Ann. der Phys. (Pogg.)*, 17 (1829), 247; 18 (1829), 331; 19 (1830), 337; *Ann. chim. phys.* 44 (1830), 189, 244; *Ann. des Mines* [3], 1 (1832), 409, 411.

- 1828: 11. G. MAGNUS. Ueber einige neue Verbindungen des Platinchlorürs. (Salt of Magnus, first platinum base.) Pt.

*Ann. der Phys. (Pogg.)*, 14 (1828), 239; *Ann. chim. phys.* 40 (1829), 110; *Quart. J. Sci.* 1 (1829), 420; *Ann. des Mines* [3], 1 (1832), 142; *Berzelius Jsb.* 9 (1830), 159; *Mag. für Pharm.* 26 (1829), 297.

- 1828: 12. J. W. DÖBEREINER. Vermischte chemische Erfahrungen über Platina. (Precipitation by zinc, decomposition of carbon monoxid by dry oxid of platinum, platinum sulfid, and platinum "feuerzeug.") Pt.

*J. für Chem. (Schweigger)*, 54 (1828), 412; *Amer. J. of Sci.* 18 (1830), 151; *Quart. J. Sci.* 2 (1829), 196; *Ann. des Mines* [3], 1 (1832), 141; *Mag. für Pharm.* 26 (1829), 298.

- 1828: 13. N. W. FISCHER. Beiträge zur näheren Kenntniss des Platins und die mit demselben in Verbindung vorkommenden Metalle, namentlich des Rhodiums und Iridiums. (Action of various reagents, zinnssalz, hydrogen sulfid, &c.) Pt, Pd, Ir, Os, Rh.

*J. für Chem. (Schweigger)*, 53 (1828), 108; *Mag. für Pharm.* 24 (1828), 394; 26 (1829), 295.

- 1828: 14. L. KRÁLOVANSZKY. Vermischte chemische Bemerkungen über Lithium. (Action of lithium on platinum.) Pt.

*J. für Chem. (Schweigger)*, 54 (1828), 232, 346.

- 1828: 15. G. WETZLAR. Beiträge zur chemischen Geschichte des Silbers. (Recognition of palladium by action of copper chlorid, p. 474.) Pd.

*J. für Chem. (Schweigger)*, 52 (1828), 466.

- 1828: 16. ———. Ueber die Wirkung zwischen Gold und Silber im starren Zustande und die Legirung von Gold und Platinum. Pt.

*Ann. der Phys. (Pogg.)*, 14 (1828), 525.

- 1828: 17. O. L. ERDMANN. Technische Anwendbarkeit des rohen Platins. Pt.

*J. techn. Chem.* 1 (1828), 362.

- 1828: 18. O. L. ERDMANN. Ueber Döbereiner's Räucherlämpchen und das Platiniren des Glases. Pt.  
J. techn. Chem. 3 (1828), 395.
- 1828: 19. O. L. ERDMANN. Seebeck's Prüfung der Platina auf ihre Reinheit durch Thermomagnetismus. Pt.  
J. techn. Chem. 2 (1828), 89.
- 1828: 20. J. ZUBER. (Platinirung.) Pt.  
Bul. Soc. Indust. Mulhouse, 4, ; J. techn. Chem. 2 (1828), 527.
- 1828: 21. LABONTÉ AND DEPUIS. (Verfahren Kupfer mit Platina zu plaquiren.) Pt.  
Descr. d. machines dans les brevets, par Christian, 1828, 523;  
Rep. of Pat. Inventions, June, 1828, 580; Polyt. J. (Dingler), 33 (1829), 129; J. Frank. Inst. [2], 6 (1830), 176.
- 1828: 22. J. S. C. SCHWEIGGER. Ueber Nobili's elektrochemischen Figuren. (Platinum plating on glass.) Pt.  
J. für Chem. (Schweigger), 54 (1828), 59.
- 1828: 23. J. P. J. D'ARCET. Ueber die Scheidung des Goldes und Silbers vom Kupfer mittelst Schwefelsäure. (Use of platinum vessels.) Pt.  
Recueil Industriel, Dec. 1828; from Mémoire on Instructions relative to the Art of Refining, Paris, 1828 (or 1827?); J. techn. Chem. 4 (1829), 424; Polyt. J. (Dingler), 31 (1828), 281; Bibl. Univ. Apr. 1829; Amer. J. of Sci. 17 (1830), 179.
- 1828: 24. K. W. G. KASTNER. Güte und Preis des Nürnberger Blatt- und Maler-Platin. Pt.  
Arch. ges. Naturl. 14 (1828), 162.
- 1828: 25. N. W. FISCHER. Zur Geschichte des Platins. (Wärmeleitung des Platins, also chlorids of ammonium and platinum.) Pt.  
Arch. ges. Naturl. 14 (1828), 145; J. techn. Chem. 3 (1828), 263;  
Quart. J. of Sci. 5 (1829), 193; Berzelius Jsb. 9 (1830), 109, 113, 161; Mag. für Pharm. 24 (1828), 347.
- 1828: 26. L. SCHWARTZ. Sur la mesure des hautes températures. Pt.  
Bul. Soc. Indust. Mulhouse, 1 (1828), 22; J. techn. Chem. 2 (1828), 341.
- 1828: 27. C. H. PFAFF. Ueber die sogenannte elektrische Ladung der Metalle im Kreise der voltaischen Säule. (No change in platinum wire.) Pt.  
J. für Chem. (Schweigger), 53 (1828), 401.
- 1828: 28. DUBLANC. (Platinum chlorid test for iodine.) Pt.  
Berzelius Jsb. 7 (1828), 148.

- 1829: 1. A. T. KUPFFER. Versuch einer geognostischen Schilderung des Urals. (Occurrence of platinum, p. 283.) Pt.  
Ann. der Phys. (Pogg.), 16 (1829), 260.
- 1829: 2. ————. Platingewinnung am Ural (Ausbeute). Pt.  
Ann. der Phys. (Pogg.), 15 (1829), 52; J. techn. Chem. 5 (1829), 104.
- 1829: 3. ————. (Platinum in Ural mts.) Pt.  
"From a Prussian Journal"; Amer. J. of Sci. 18 (1830), 190; Phil. Mag. [2], 7 (1830), 59; Bibl. Univ. July, 1829 [1830?].
- 1829: 4. J. C. L. ZINCKEN. Ueber das Palladium im Herzogthum Anhalt-Bernburg. Pd.  
Ann. der Phys. (Pogg.), 16 (1829), 491; J. techn. Chem. 6 (1829), 235; J. für Chem. (Schweigger), 56 (1825), 487; Ann. chim. phys. 44 (1830), 206; Ann. des Mines [3], 1 (1832), 447; Berzelius Jsb. 10 (1831), 167; 11 (1832), 202.
- 1829: 5. BENECKE AND RIENECKER. Ueber das Selen-Palladium bei Tilkerode im Harze. (Arbeit.) Pd.
- 1829: 6. G. OSANN. Berichtigung, meine Analyse des ural'schen Platins betreffend. (No new metal present.)  
[Ru, Po, Plu,] Pt, Pd, Ir, Os, Rh.  
Ann. der Phys. (Pogg.), 15 (1829), 158; Arch. ges. Naturl. 16 (1829), 129; Mag. für Pharm. 26 (1829), 294.
- 1829: 7. W. H. WOLLASTON. Sur la préparation du palladium. Pd.  
Ann. chim. phys. 41 (1829), 413.
- 1829: 8. W. H. WOLLASTON. Sur la préparation de l'osmium. Os.  
Ann. chim. phys. 41 (1829), 414.
- 1829: 9. J. J. BERZELIUS. Einige nachträgliche Bemerkungen über das Iridium und das Osmium. (Continued from 1828: 9.) Ir, Os.  
Ann. der Phys. (Pogg.), 15 (1829), 208; Ann. chim. phys. 42 (1829), 185; Ann. des Mines [3], 1 (1832), 144.
- 1829: 10. W. C. ZEISE. Om Platin chloridet. Havniae (Copenhagen), 1830. Pt.  
Oversigt. Danske Vid. Sels. 1829-30, 21; Afhandl. Danske Vid. Sels. 5 (1832), 55.
- 1829: 11. [E.] DAVY. Fulminic acid. Pt.  
Roy. Soc. Dublin, 1829; Berzelius Jsb. 12 (1833), 95, 121; Pharm. Centrbl. 1835, 8.
- 1829: 12. J. J. BERZELIUS. Eine besondere Art von Platinsalzen. (Organic platinum compound, probably "Acechlorplatin" of Zeise.) Pt.  
Berzelius Jsb. 9 (1830), 162; Ann. der Phys. (Pogg.), 16 (1829), 82; Mag. für Pharm. 28 (1829), 316.

- 1829: 13. J. L. LASSAIGNE. Sur les combinaisons de l'iode avec le manganèse, le fer, et le platine. Pt.  
J. chim. méd. 5 (1829), 330; Ann. des Mines [3], 1 (1832), 114; Berzelius Jsb. 10 (1831), 152.
- 1829: 14. K. W. G. KASTNER. Unerwartetes Reduction der aufgelösten Platinoxys, durch Aether. Pt.  
Arch. ges. Naturl. 18 (1829), 388.
- 1829: 15. L. H. ZENNECK. Ueber das pneumatische Verhalten einiger Metalle zur Salzsäure. (Platinum in hydrochloric acid, p. 101.) (Platinum foil helps solution of metals in hydrochloric acid, p. 108.) Pt.  
Arch. ges. Naturl. 17 (1829), 92.
- 1829: 16. W. A. LAMPADIUS. Einige neue Erfahrungen über das Verhalten des Silbers gegen Platin. (Alloy and separation.) Pt.  
J. techn. Chem. 4 (1829), 279; Ann. des Mines [3], 1 (1832), 412.
- 1829: 17. W. A. LAMPADIUS. Zerlegung der Iridchloride durch Platinmetalle. (Also iridium alloys and separation.) Pt, Ir.  
J. techn. Chem. 6 (1829), 453; 11 (1831), 1; Ann. des Mines [3], 1 (1832), 412.
- 1829: 18. N. W. FISCHER. Ueber Metallsuperoxyde. (Palladium superoxyd, p. 218.) Pd.  
Arch. ges. Naturl. 16 (1829), 214; Mag. für Pharm. 28 (1829), 317.
- 1829: 19. N. W. FISCHER. Ueber die Wiederherstellung der Metalle durch Stickstoff. (Reduction of palladium on evaporation by the nitrogen of the air; also observations (p. 459) by Kastner.) Pt, Pd.  
Arch. ges. Naturl. 18 (1829), 105, 457; Ann. der Phys. (Pogg.), 17 (1829), 137, 479; Amer. J. of Sci. 19 (1831), 371.
- 1829: 20. W. H. WOLLASTON. On a method of rendering platina malleable. (Bakerian Lecture, 1828.) (Also palladium, and the obtaining of the oxid of osmium in a crystalline state.) Pt, Ir, Os, Pd.  
Phil. Trans. London, 119 (1829), 1; Proc. Roy. Soc. London, 2 (1833), 352; Ann. chim. phys. 41 (1829), 403; J. techn. Chem. 5 (1829), 235; 6, 221; Ann. der Phys. (Pogg.), 15 (1829), 299; 16, 158; J. für Chem. (Schweigger), 55 (1829), 376; 56, 253; 57, 69; Phil. Mag. [2], 5 (1829), 65; 6, 1; Polyt. J. (Dingler), 31 (1829), 76; 32, 149; 34, 1; Quart. J. of Sci. 6 (1829), 97; J. Frank. Inst. [2], 4 (1829), 226; Bibl. Univ. 41 (1829), 128; Mech. Mag. 279 (1828), 319; Arch. ges. Naturl. 17 (1829), 113; Berzelius Jsb. 9 (1830), 107; Mag. für Pharm. 28 (1829), 314.



- 1829: 21. J. N. PLANIÁVÁ. Bereitung eines leicht zündenden Platinschwammes. Pt.  
Ztsch. für Phys. (Baumgartner), 5 (1829), 9; J. techn. Chem. 4 (1829), 121.
- 1829: 22. J. VON LIEBIG. Sur le précipité noir de platine de M. Edmund Davy, et sur la propriété de l'éponge de platine d'enflammer l'hydrogène. Pt.  
Ann. chim. phys. 42 (1829), 316; Amer. J. of Sci. 18 (1830), 398; Ann. der Phys. (Pogg.), 17 (1829), 101; J. techn. Chem. 6 (1829), 467; J. Frank. Inst. [2], 6 (1830), 269.
- 1829: 23. F. WÖHLER. Increased combustibility of carbon by platinum. Pt.  
Quart. J. of Sci. 6 (1829), 178; Phil. Mag. [2], 6 (1829), 394.
- 1829: 24. J. W. DÖBEREINER. Zur weiteren Kenntniss der chemischen Dynamik des Platins, etc. (Platiniren des Glases.) (Quantitative Bestimmung des Alkohols mittelst Platinsuboxydul.) Pt.  
Arch. ges. Naturl. 16 (1829), 111; J. techn. Chem. 4 (1829), 496; 5 (1829), 103; Berzelius Jsb. 10 (1831), 111.
- 1829: 25. T. GRAHAM. On the application of spongy platinum to eudiometry. Pt.  
Quart. J. Sci. 2 (1829), 354; J. techn. Chem. 8 (1830), 20; Bibl. Brit. [2], 43 (1830), 387.
- 1829: 26. A. C. BECQUEREL. De pouvoir thermo-électrique des métaux. (Copper-platinum and iron-platinum couples.) Pt.  
Ann. chim. phys. 41 (1829), 353; Mém. de l'Inst. Paris, 10 (1831), 237; Ann. der Phys. (Pogg.), 16 (1829), 306; 17, 535; J. für Chem. (Schweigger), 57 (1829), 302.
- 1829: 27. C. DESPRETZ. Observations sur les modifications que subissent les métaux dans leurs propriétés physiques, par l'action combinée du gaz ammoniacal et de la chaleur. (No change in platinum, p. 129.) Pt.  
Ann. chim. phys. 42 (1829), 122; Ann. der Phys. (Pogg.), 17 (1829), 296; J. für Chem. (Schweigger), 58 (1830), 226; Quart. J. of Sci. 1 (1830), 201.
- 1830: 1. M. VON ENGELHARDT. Die Lagerstätte der Diamanten im Ural-Gebirge. Riga, 1830. (Occurrence of platinum.) Pt.  
Arch. ges. Naturl. 21 (1831), 160.
- 1830: 2. M. VON ENGELHARDT. Vorkommen des Platins in dem Porphyr. Pt.  
Ann. der Phys. (Pogg.), 20 (1830), 532.

- 1830: 3. C. M. MARX. Ueber die von Struve'sche Mineralien-sammlung. (Description of platinum and iridosmium.) Pt, Os, Ir.  
Arch. ges. Naturl. 19 (1830), 370.
- 1830: 4. A. VON HUMBOLDT. (Platin-Ausbeute.) Pt.  
Ann. der Phys. (Pogg.), 18 (1830), 273; Arch. ges. Naturl. 21 (1831), 161.
- 1830: 5. QUESNEVILLE, FILS. Une methode pour separer l'osmium et l'iridium de la mine de platine. (Read at Soc. de Pharm., Aug. 11, 1830.) Pt, Ir, Os.  
J. chim. méd. 6 (1830), 668; J. de Pharm. 16 (1830), 557; Polytechn. (Dingler), 40 (1831), 73; Berzelius Jsb. 11 (1832), 144.
- 1830: 6. J. J. BERZELIUS. Oxyde des Platins. Pt.  
Berzelius Jsb. 9 (1830), 110.
- 1830: 7. J. VON LIEBIG. Neue Erfahrungen über J. [!E.] Davy's sogenanntes salpetrichtsaures Platinoxyd oder Döbereiner's Platinsuboxyd. Pt.  
Mag. für Pharm. 29 (1830), 101.
- 1830: 8. L. HÜNEFELD. Ueber zwei neue Doppelsalze aus Chlor, Zink und Platin. (Zinc platino- and platini-chlorid.) Pt.  
J. für Chem. (Schweigger), 60 (1830), 197; Arch. ges. Naturl. 21 (1831), 471; Berzelius Jsb. 11 (1832), 191.
- 1830: 9. N. W. FISCHER. Bemerkungen über die Platinmetalle. (Phosphorsaures Rhodiumoxyd u. s. w.) Pt, Pd, Os, Ir, Rh.  
J. für Chem. (Schweigger), 18 (1830), 256; Berzelius Jsb. 11 (1832), 143; Mag. für Pharm. 32 (1830), 314.
- 1830: 9a. —————. Seleniuret of palladium. Pd.  
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- 1830: 10. G. F. WACH. Ueber das Phänomen, welches von Dutrochet mit dem Ausdrucke Endosmose und Exosmose bezeichnet wurde, und daran sich reihende Beobachtungen über Metallvegetationen. ("Platinvegetation.") Pt.  
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- 1830: 11. G. OSANN. (Specific gravity of platinum, etc.) Pt.  
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- 1830: 12. K. W. G. KASTNER. Vervollkommnung des Platin-schwamms. Pt.  
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- 1830: 13. M. FARADAY. On the manufacture of glass for optical purposes (Bakerian Lecture, 1829). (Use of platinum for vessels, p. 16; preparation of spongy platinum, p. 56.) Pt.  
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- 1830: 14. W. A. LAMPADIUS. Einfaches Verfahren Kupfer und Messing mit Silber und Platin zu bedecken. Pt.  
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- 1830: 15. J. F. DANIELL. On certain phenomena resulting from the action of mercury upon different metals. (Mercury on platinum.) Pt.  
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- 1830: 16. F. GOBEL. Magnetische Reaction des Platins. Pt.  
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- 1830: 17. ————. (Imitation of platinum by copper zinc alloy.) Pt.  
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- 1830: 18. W. E. WEBER. Ueber die specifische Wärme fester Körper, insbesondere der Metalle. Pt.  
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- 1830: 19. N. W. FISCHER. Zur Wärmelehre, besonders in Hinsicht auf das Leitungsvermögen des Platins. Pt.  
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- 1831: 1. ————. On the gold, silver, and platina of Russia. Pt.  
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- 1831: 2. J. N. FUCHS. Platingeschiebe von ausserordentlicher Grösse von Nische Tagilsk. Pt.  
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- 1831: 3. ————. Verkauf von Osmium Iridium. (Price.) Os, Ir. Pt.  
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- 1831: 4. W. C. ZEISE. Von der Wirkung zwischen Platinchlorid und Alkohol, und von den dabei entstehenden neuen Substanzen. Pt.  
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- 1831: 5. W. C. ZEISE. Kulbrintet Chlorplatin-ammoniak [1831].  
(Gekohlenwasserstofftes Chlorplatin-Ammoniak.) Pt.  
Afhandl. Danske Vid. Sels. 5 (1832), 141; Oversigt. Danske Vid.  
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- 1831: 6. A. CONNELL. On the acidification of iodine by means of  
nitric acid. (Iodic acid has no action on platinum.) Pt.  
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- 1831: 7. A. C. BECQUEREL. Du carbonate de chaux cristallisé, et de  
l'action simultanée des matières sucrées ou mucilagineuses sur  
quelques oxides métalliques, par l'intermédiaire des alcalis et des  
terres. (Action on oxid of platinum.) Pt.  
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- 1831: 8. J. W. DÖBEREINER. Zersetzung des Platinchlorids von  
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383.
- 1831: 9. J. W. DÖBEREINER. Ueber Oxal-, Ameisen-, und Essigsäure.  
(Action of platinum black.) Pt.  
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- 1831: 10. F. W. SCHWEIGGER-SEIDEL. Nachtrag zu Döbereiner's  
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- 1831: 11. F. W. SCHWEIGGER-SEIDEL. Ueber Platinaghlühlampen und  
Lampenessig. Pt.  
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- 1831: 12. J. W. DÖBEREINER. Ueber Platinmohr und einen Essig-  
bildungs-Apparat. Pt.  
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- 1831: 13. J. W. DÖBEREINER. Ueber Entzündung des Knallgases  
durch Platinmohr. Pt.  
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114.
- 1831: 14. J. W. DÖBEREINER. Ueber Iridmohr und dessen ausge-  
zeichnete Zündkraft. Ir.  
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- 1831: 15. J. W. DÖBEREINER. Portatives Iridfeuerzeug. Ir.  
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- 1831: 16. J. W. DÖBEREINER. Merkwürdige Ammoniakbildung (aus Salpetersäure, Alkohol und Platin- oder Irid-mohr). Pt, Ir.  
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- 1831: 17. J. W. DÖBEREINER. Ueber Nobili's elektro-chemische Farbenfiguren. Pt.  
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- 1831: 18. R. BÖTTGER. Ueber Platinaschwamm und die, dessen Zündkraft völlig aufhebende, Eigenschaft der, mit Ammoniakgas vermischten, atmosphärischen Luft. Pt.  
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- 1831: 19. J. S. C. SCHWEIGGER. Ueber Böttger "über Platina-schwamm, u. s. w." (Action of ammonia.) Pt.  
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- 1831: 20. H. HESS. Sur le propriété que possède le platine très divisé d'opérer la combinaison de l'oxygène avec l'hydrogène, et sur la densité du platine. Pt.  
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- 1831: 21. R. HARE. Asbestos impregnated with platinum. (Letter.) Pt.  
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- 1831: 22. G. MERRYWEATHER. Account of a platina lamp. Pt.  
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- 1831: 23. S. F. HERBSTÄDT. Versuche und Beobachtungen über die Essigsäure. (Action of platinum black on alcohol.) Pt.  
Abhand. Acad. Berlin. 1831, 285; J. techn. Chem. 17 (1833), 232; Pharm. Centrbl. 1833, 587.
- 1831: 24. J. A. BUCHNER. (Action of fused ammonium nitrate on platinum.) Pt.  
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- 1831: 25. J. J. BERZELIUS. Vanadins föreningar med metaller. (Platinum-vanadium alloy.) Pt.  
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- 1831: 26. STIEREN. Platingefässe. Pt.  
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- 1831: 27. H. ABICH. Chemische Untersuchung des Spinels. (Steel press for platinum, p. 309.) Pt.  
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- 1831: 28. J. F. DANIELL. Further experiments with a new register pyrometer for measuring the expansion of solids. (Cause of change of texture of platinum when heated with black lead, p. 456.) Pt.  
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- 1831: 29. BOUDON DE ST. AMAND. Platin in Porcellanfärbung u. s. w. Pt.  
Desc. d. Machines, Brevets d'Inv. par Christian, 16, 5; Polyt. J. (Dingler), 41 (1831), 219.
- 1832: 1. ———. Platinausbeute am Ural. Pt.  
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- 1832: 2. J. F. W. HERSCHEL. On the action of light in determining the precipitation of muriate of platinum by limewater. Pt.  
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- 1832: 3. J. W. DÖBEREINER. Ueber Platinoxyd-Natron und daraus bereiteten Platinmohr. Pt.  
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- 1832: 4. P. A. VON BONSDORFF. Analys af tvenne Brom-salter (Bromo-Platinas Natricus och Bromo-Auras Kalicus.) Pt.  
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- 1832: 5. J. L. LASSAIGNE. Mémoire sur les iodures de platine et les composés doubles qu'ils peuvent former avec les iodures basiques, l'acide hydriodique, et l'hydriodate d'ammoniaque. Pt.  
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- 1832: 6. J. L. LASSAIGNE. Recherches sur la limite de sensibilité de certains réactifs très-employés dans l'analyse chimique. (Platinic chlorid.) Pt.  
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- 1832: 7. P. ORFILA. Ueber mehrere mineralische Gifte. (Platinic chlorid for potassium iodid.) Pt.  
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- 1832: 8. R. J. KANE (and R. PHILLIPS). Analysis of some compounds of platinum. (Iodids.) (Observations by R. Phillips in Phil. Mag. 2: 197.) Pt.  
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- 1832: 9. J. W. DÖBEREINER. Notizen über Sauerstoffäther, und verwandte Gegenstände. (Action of platinum black in promotion of the oxidation of sulfur dioxid to sulfuric acid.) Pt.  
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- 1832: 10. J. W. DÖBEREINER. Ueber die depotenzirende Wirkung des Ammoniaks auf den Platinschwamm. Pt.  
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- 1832: 11. J. W. DÖBEREINER. Ueber die Bereitung des Platinmohrs. Pt.  
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- 1832: 12. ————. Ueber Essigsäureerzeugung. (Use of platinum black.) (Subject of a prize award.) Pt.  
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- 1832: 13. P. PHILLIPS. Ueber Fabrication der Schwefelsäure ohne Salpeter. (By platinum black.) Pt.  
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- 1832: 14. ————. Bereitung und interessanteste Eigenschaften verschiedener merkwürdiger Platinpräparate nebst darauf gegründeten Apparaten und Versuchen. (Chiefly on action of platinum black.) Pt, Ir.  
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- 1832: 15. W. MARSHALL. An account of the Russian method of rendering platinum malleable. Pt.  
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- 1832: 16. C. M. MARX. Die Schweissbarkeit des Platins. Pt.  
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- 1832: 17. J. J. BERZELIUS. Ueber verschiedene chemische Operationen und Geräthschaften. (Platinum crucibles, p. 357.) Pt.  
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- 1832: 18. G. BISCHOF. Leichte Zerstörbarkeit von Platingefässen. Pt.  
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- 1832: 19. ————. (Platinum alloys.) Pt.  
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- 1833: 1. G. ROSE. Ueber die im Ural vorkommenden krystallisirten Verbindungen von Osmium und Iridium. Ir, Os.  
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- 1833: 2. ————. Gisement du platine en Sibérie. Pt.  
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- 1833: 3. H. F. GAULTIER DE CLAUVERY. (Discovery of platinum in France in galena.) Pt.  
Soc. d'Encouragement, May 8, 1833; Polyt. J. (Dingler), 49 (1833), 232; L'Institut ; J. chim. méd. 9 (1833), 434.
- 1833: 4. DANGAZ. (Platinum in France; with analysis.) Pt.  
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- 1833: 5. D'ARGY. Platine en galène. (Discovery of platinum in France.) Pt.  
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- 1833: 6. J. PRINSEP. Note on the discovery of platina in Ava. Pt.  
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- 1833: 7. W. A. LAMPADIUS and G. P. PLATTNER. Ueber das gemeinschaftliche Vorkommen des Platinerzes und des gediegenen Silbergoldes in einem Gangfossile aus Brasilien. Pt.  
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- 1833: 9. J. J. BERZELIUS. Undersökning af Osmium-Iridium. Os, Ir.  
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- 1833: 10. A. BREITHAUP. Ueber einen Körper, der schwerer als Platin ist. (Osmiridium; also specific gravity of palladium.) Os, Ir, Pd.  
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- 1833: 11. A. BREITHAUP. Vorläufige chemische Untersuchungen des schwersten metallischen Körpers, den man kennt. (Osmiridiums.) Os, Ir.  
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- 1833: 12. J. PERSOZ. (Separation of osmium and iridium.) Os, Ir.  
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- 1833: 13. J. J. BERZELIUS. Atomgewichte der einfachen Körper. Pt, Pd, Ir, Rh, Os.  
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- 1833: 14. R. PHILLIPS. Experiments on platina. (Reduction by tartrates, etc.) Pt.  
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- 1833: 15. J. W. DÖBEREINER. Ueber mehrere neue Platinverbindungen. (Oxalsures Platin, und Platinsuren Natron.) Pt.  
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- 1833: 16. J. L. LASSAIGNE. Sur l'iodure de palladium. Pd.  
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- 1833: 17. R. J. KANE. Remarks on the composition of the iodide of platinum. Pt.  
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- 1833: 18. R. J. KANE. Réclamation au sujet de la découverte des iodures de platine. Pt.  
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- 1833: 19. J. L. LASSAIGNE. Réponse à M. R. J. Kane. (On discovery of iodids of platinum.) Pt.  
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- 1833: 20. R. PHILLIPS. Observations on Mr. R. J. Kane's "Analysis of some combinations of platinum" (iodids). cf. (1832: 8). Pt.  
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- 1833: 21. F. GÖBEL. Verhalten der Ameisensäure zu einigen Metalloxyden und Hyperoxyden. (Action on oxids of platinum and palladium.) Pt, Pd.  
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- 1833: 22. J. B. BOUSSINGAULT. Examen d'une substance considérée comme un composé d'hydrogène et de platine. Pt.  
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- 1833: 23. R. BÖTTGER. Einige Bemerkungen über Bereitungs- und Behandlungsweise des Platinschwammes zum Gebrauch in Döbereiner's Apparat zur Entzündung des Hydrogens. Pt.  
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- 1833: 24. A. F. E. DEGEN. Ueber ein Eudiometer, bei dem die Wasserbildung durch unvermischten Platinschwamm bewirkt wird. Pt.  
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- 1833: 25. J. L. PREVOST. (Salzsaures Natron-Platin als Heilmittel in der Epilepsie.) Pt.  
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- 1833: 26. G. F. C. FRICK. Ueber die Anwendung des Iridiums zu Porcellanfarben. Ir.  
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- 1833: 27. E. LENZ. Ueber die Leitungsfähigkeit der Metalle für die Electricität, bei verschiedenen Temperaturen. Pt.  
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- 1834: 1. P. BERTHIER and A. C. BECQUEREL. Platin in Frankreich. Ann. der Phys. (Pogg.), 31 (1834), 590. Pt.
- 1834: 2. VILLAIN. (Platinum in France.) Pt.  
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- 1834: 3. ———. Platinum in France. Pt.  
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- 1834: 4. G. ROSE. Ueber die Lagerstätte des Platins im Ural. Pt.  
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- 1834: 5. E. F. COOKE. Price of platinum. Pt.  
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- 1834: 6. L. F. SVANBERG. Bidrag till närmare kännedom af kemiske sammansättningen af de Amerikanska platinamalmerne. (Composition of Platina del Pinto and other South American platinum and iridium.) Pt, Pd, Ir, Os, Rh.  
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- 1834: 7. P. SOBOLEVSKY. Ueber das Ausbringen des Platins in Russland. Pt.  
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- 1834: 8. F. WÖHLER. Ueber die Gewinnung von Iridium und Osmium aus dem Platinrückstand. (Heating with sodium chlorid in chlorin.) Pt, Pd, Ir, Os, Rh.  
Ann. der Phys. (Pogg.), 31 (1834), 161; Ann. Chem. (Liebig), 9 (1834), 149; Amer. J. of Sci. 26 (1834), 371; Ztsch. anal. Chem. 5 (1866), 121; Berzelius Jsb. 15 (1836), 145; Pharm. Centrbl. 1834, 207.
- 1834: 9. J. PERSOZ. Mémoire sur la préparation de l'osmium et de l'iridium, et sur l'action du sulfate acide de potasse sur les métaux de platine en présence des chlorures alcalins. (Also decomposition by sodium sulfid.) Pt, Pd, Ir, Os, Rh.  
Ann. chim. phys. 55 (1834), 210; Ann. Chem. (Liebig), 12 (1834), 12; 16 (1835), 204; J. prakt. Chem. 2 (1834), 473; Phil. Mag. [3], 5 (1834), 314; Polyt. J. (Dingler), 53 (1834), 129; Ztsch. anal. Chem. 5 (1866), 120.

- 1834: 10. R. BÖTTGER. Neues Verfahren, aus den Chloriden des Platins und Iridiums, mittelst flüssigen Schwefelkohlenstoffs, Schwefelplatin und Schwefeliridiums darzustellen. Pt, Ir.  
J. prakt. Chem. 3 (1834), 267; Ann. Chem. (Liebig), 16 (1835), 206; Berzelius Jsb. 15 (1836), 148, 153, 154.
- 1834: 11. R. J. KANE. On some compounds formed by the action of [proto]chloride of platinum and [proto]chloride of tin. Pt.  
Dublin J. Med. Chem. Sci. 5 (1834).
- 1834: 12. W. C. ZEISE. Om mercaptanet. (Platinmercaptid.) Pt.  
Afh. Dansk. Vid. Sels. 6 (1837), 1; J. prakt. Chem. 1 (1834), 409.
- 1834: 12a. J. C. BOOTH. (Potassium iridium cyanid.) Ir.  
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- 1834: 13. J. VON LIEBIG. Ueber die Constitution des Aethers und seiner Verbindungen. (Entzündliches Platinchlorür von Zeise, p. 9.) Pt.  
Ann. Chem. (Liebig), 9 (1834), 1; Ann. der Phys. (Pogg.), 31 (1834), 321.
- 1834: 14. J. J. BERZELIUS. Atomgewichte der einfachen Körper. Pt, Pd, Ir, Os, Rh.  
Pharm. Centrbl. 1834, 2.
- 1834: 15. R. BRANDES. Reagens für Weinsteinsäure. (Platinic chlorid.) Pt.  
Ann. Chem. (Liebig), 9 (1834), 302; Pharm. Centrbl. 1834, 670.
- 1834: 16. K. W. G. KASTNER. Chemikalische Bemerkungen. (Kalium platinichlorid als Zeugdruckfarbe, p. 408; Zusatz von Weingeist zur Reinigung des Platinchlorids und des Iridiumchlorids, p. 409.) Pt, Ir.  
Arch. ges. Naturl. 26 (1834), 407.
- 1834: 17. P. BERTHIER. "Traité des essais par la voie sèche." Vol. 2, p. 1002. Ir, Os.  
Ann. des Mines [3], 5 (1834), 490; Berzelius Jsb. 15 (1836), 148.
- 1834: 18. L. F. BLEY. Platinmohr. Pt.  
J. prakt. Chem. 2 (1834), 520; Pharm. Centrbl. 1835, 15.
- 1834: 19. M. FARADAY. On the power of metals and other solids to induce the combination of gaseous bodies. Pt, Pd, Ir, Os, Rh.  
Phil. Trans. London, 124 (1834), 55; Ann. Chem. (Liebig), 14 (1835), 1; Ann. der Phys. (Pogg.), 33 (1834), 151; J. de Pharm. 21 (1835), 36; Polyt. J. (Dingler), 51 (1834), 274; Pharm. Centrbl. 1835, 458; Lit. Gazette, No. 888; Phil. Mag. 5 (1834), 161, 252, 334, 424; Ann. des Mines [3], 7 (1835), 483.

- 1834: 20. J. W. DÖBEREINER. Sauerstoffabsorption des Platins. Pt.  
Ann. der Phys. (Pogg.), 31 (1834), 512, aus Preus. Staatsztg.  
Mar. 13, 1834; Ann. Chem. (Liebig), 12 (1834), 236; Bibl. Brit.  
[2], 56 (1834), 332; Ann. des Mines [3], 7 (1835), 485.
- 1834: 21. J. W. DÖBEREINER. Ausserordentliche Verdichtung des  
Sauerstoffs durch Platinmohr. Pt.  
J. prakt. Chem. 1 (1834), 76.
- 1834: 22. J. W. DÖBEREINER. Ueber Platinmohr. Pt.  
J. prakt. Chem. 1 (1834), 254; Pharm. Centrbl. 1834, 50.
- 1834: 23. J. W. DÖBEREINER. Das Platin als reines Oxyrrhodon  
(Sauerstoffgassauer) erkannt. Pt.  
J. prakt. Chem. 1 (1834), 114, 369; Berzelius Jsb. 15 (1836), 151;  
Pharm. Centrbl. 1834, 477, 509.
- 1834: 24. R. BÖTTGER. Fernere Ergebnisse meiner Versuche über  
Bildung einiger Amalgame. (Platinamalgame.) Pt.  
J. prakt. Chem. 3 (1834), 278; Pharm. Centrbl. 1835, 105.
- 1834: 25. K. KARMARSH. Versuche über die absolute Festigkeit der  
(zu Draht gezogenen) Metalle. Pt.  
Jahrb. Polyt. Inst. Wien. 18 (1834), 54; Pharm. Centrbl. 1834, 337.
- 1835: 1. ————. Platina and gold of the Uralian Mountains. Pt.  
Edinb. N. Phil. J. 18 (1835), 366; Amer. J. of Sci. 28 (1835), 395.
- 1835: 2. TEPLOFF. Aperçu de la richesse minérale de l'empire Russe.  
(Occurrence of platinum.) Pt.  
Ann. des Mines [3], 8 (1835), 51; Ann. chim. phys. 60 (1835), 394.
- 1835: 3. J. J. BERZELIUS. (Vorkommen des Platins in Ava und am  
Harz.) Pt, Pd.  
Ann. der Phys. (Pogg.), 34 (1835), 381.
- 1835: 4. L. HOPFF. Platin im Rheinsande. Pt.  
Arch. ges. Naturl. 27 (1835), 394.
- 1835: 5. J. J. BERZELIUS. Analyse des "Ouro poudre" (faules Gold)  
von Süd Amerika. Pd.  
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514.
- 1835: 6. G. ROSE. Ueber das gediegene Iridium. Ir.  
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- 1835: 7. G. OSANN. Platin mit Meteoreisen. (Is platinum meteoric?)  
Ann. der Phys. (Pogg.), 38 (1836), 238. Pt.

- 1835: 8. ————. Product of platinum mines. Pt.  
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- 1835: 9. F. DÖBEREINER. Ueber eine neue Methode der Analyse des Platinerzes, der Darstellung des Platinmohrs und des chemisch reinen Palladiums. Pt, Pd.  
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- 1835: 10. J. R. JOSS. Wichtige Bemerkung als Beitrag zur Zerlegung des Osmium-Irids. Pt, Ir, Os, Rh.  
J. prakt. Chem. 4 (1835), 371.
- 1835: 11. J. W. DÖBEREINER. Fernere Mittheilungen [über Osmium-Irid, platinsäuren Kalk und Platinoxynatron]. Pt, Os, Ir.  
Ann. der Phys. (Pogg.), 36 (1835), 464; J. Frank. Inst. [2], 26, (1840), 196; Ann. des Mines [3], 15 (1839), 445; Bibl. Univ. 4 (1836), 167.
- 1835: 12. J. W. DÖBEREINER. Chemische Eigenschaften und physikalische Natur des auf nassem Wege reducirten Platins. (Reaction between platinum chlorid and ferric chlorid, &c.) (Ann. Chem. (Liebig) 14 : 15; also by F. Döbereiner and Weiss.) Pt.  
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- 1835: 13. J. R. JOSS. Ueber eine merkwürdige Reduction des Platins. Pt.  
J. prakt. Chem. 4 (1835), 374.
- 1835: 14. W. W. MATHER. Crystallized perchloride of platinum. Pt.  
Amer. J. of Sci. 27 (1835), 262.
- 1835: 15. W. W. MATHER. Iodide of potassium and platinum. Pt.  
Amer. J. of Sci. 27 (1835), 257.
- 1835: 16. R. J. KANE. On some combinations of protochloride of platinum with protochloride of tin. Pt.  
Brit. Ass. Rept. 1835, ii, 44; Phil. Mag. [3], 7 (1835), 399; Ann. Chem. (Liebig), 20 (1836), 187; J. prakt. Chem. 7 (1836), 135; Pharm. Centrbl. 1836, 301.
- 1835: 17. J. L. LASSAIGNE. Mémoire sur les combinaisons de l'iode avec le palladium et l'iridium. Pd, Ir.  
J. chim. méd. [2], 1 (1835), 57; Pharm. Centrbl. 1835, 202; Berzelius Jsb. 16 (1837), 153.

- 1835: 18. J. J. BERZELIUS. Atomgewichte der einfachen Körper.  
(Atomic weight of platinum metals.) Pt, Pd, Rh, Ir, Os.  
Pharm. Centrbl. 1835, 1.
- 1835: 19. W. MAUGHAM. (Fusion of platinum by the oxyhydrogen  
blowpipe.) Pt.  
Soc'y of Arts, May 12 (1835); Mag. of Pop. Sci. 3 (1837), 208;  
Polyt. J. (Dingler), 61 (1836), 75.
- 1835: 20. W. W. MATHER. Amalgam of platinum. Pt.  
Amer. J. of Sci. 27 (1835), 263.
- 1835: 21. J. VON LIEBIG. Ueber die Producte der Oxydation des Alko-  
hols. (Oxydation of alcohol by means of platinum sponge.) Pt.  
Ann. Chem. (Liebig), 14 (1835), 133; Ann. chim. phys. 59 (1835),  
289; J. de Pharm. 21 (1835), 472; Ann. der Phys. (Pogg.), 36  
(1835), 275; Pharm. Centrbl. 1835, 649.
- 1835: 22. W. ARTUS. Ueber die Vernichtung der Zündkraft des  
Platinschwammes durch Schwefelwasserstoffgas. Pt.  
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- 1835: 23. G. F. HÄNLE. Verbesserung an den Platinfenerzeugen. Pt.  
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633.
- 1835: 24. W. C. HENRY. Experiments on the action of metals in de-  
termining gaseous combination. (Action of platinum.) Pt.  
Phil. Mag. [3], 6 (1835), 362; Ann. der Phys. (Pogg.), 36 (1835),  
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348; Edinb. N. Phil. J. (1836), 99; Pharm. Centrbl. 1835, 838;  
Ann. des Mines [3], 9 (1835), 383.
- 1836: 1. R. HERMANN. Ueber Irit und Osmir, zwei neue Mineralien.  
Bul. Soc. Nat. Moscow, 9 (1836), 215. Ir, Os.
- 1836: 2. J. E. HERBERGER. (Silber haltiges Platin.) Pt.  
Repert. für Pharm. (Buchner) [2], 5 (1836), 211; Ann. Chem.  
(Liebig), 20 (1836), 186; Pharm. Centrbl. 1836, 477.
- 1836: 3. R. HERMANN. Ueber einige dreifache Verbindungen von  
Osmium-, Iridium- und Platinchlorid mit Chlorkalium und  
Chlorammonium. Pt, Ir, Os.  
Ann. der Phys. (Pogg.), 37 (1836), 407; Bibl. Univ. 4 (1836), 384;  
Phil. Mag. [3], 9 (1836), 232; Pharm. Centrbl. 1836, 364; Ann.  
des Mines [3], 11 (1837), 276.
- 1836: 4. J. W. DÖBEREINER. Ueber mehrere neue Platinverbindun-  
gen. (Cyanids of platinum, platinum and mercury, and platinum  
and hydrogen.) Pt, Ir.  
Ann. der Phys. (Pogg.), 37 (1836), 545; Ann. Chem. (Liebig), 17  
(1836), 250; J. de Pharm. 22 (1836), 551; Phil. Mag. [3], 9

(1836), 314; Pharm. Centrbl. 1836, 417; Bul. Univ. 4 (1836), 381; Ann. des Mines [3], 11 (1837), 273.

- 1836: 5. W. C. ZEISE. Ny undersögelse over det braenbare Chlorplatin. (Combustible chlorid of platinum with alcohol.) Pt.

Afhand. Danske Vid. Sels. [4], 6 (1837), 333; Oversigt. Danske Vid. Sels. 1836-37, 9; Ann. chim. phys. 63 (1836), 411; Ann. Chem. (Liebig), 23 (1837), 1; Ann. der Phys. (Pogg.), 40 (1837), 234; Berzelius Jsb. 18 (1839), 445.

- 1836: 6. L. A. BUCHNER, JR. Ueber der Gränzen der Wahrnehmbarkeit mehrer chemischer Reactionen. (Platinum with stannous chlorid, mercurous nitrate and potassium iodid.) Pt.

Pharm. Centrbl. 1836, 434.

- 1836: 7. V. REGNAULT. Recherches relatives à l'action de la vapeur d'eau à une haute température sur les métaux. (Osmium, p. 366; other platinum metals, p. 368.) Pt, Pd, Ir, Os, Rh.

Ann. chim. phys. 62 (1836), 337; Ann. des Mines [3], 11 (1837), 3; J. prakt. Chem. 10 (1837), 139; J. de Pharm. 23 (1837), 185.

- 1836: 8. J. W. DÖBEREINER. Ueber eine sehr leichte Darstellung von Platinschwarz. Pt.

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- 1836: 9. J. W. DÖBEREINER. Ueber Platinmohr. Pt.

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- 1836: 10. W. C. HENRY. On gaseous interference (with water forming action of platinum). Pt.

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- 1836: 11. C. F. MOHR. Ueber die Herstellung der Zündkraft des Platinschwämmchen. Pt.

Ann. Chem. (Liebig), 18 (1836), 55; Berzelius Jsb. 17 (1838), 110.

- 1836: 12. A. F. E. DEGEN. Versuche über die Netzbarkeit der Oberfläche verschiedener Körper. (Absorption of gases by platinum.) Pt.

Ann. der Phys. (Pogg.), 38 (1836), 449; Pharm. Centrbl. 1836, 695.



- 1836: 13. A. F. E. DEGEN. Wasserbildendefähigkeit des Platins. Pt.  
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- 1836: 14. J. W. DÖBEREINER. Zur Chemie des Platins in wissenschaftlicher und technischer Beziehung, Stuttgart, 1836. Pt.  
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- 1836: 15. J. B. TROMMSDORFF. Kritik von J. W. Döbereiner's "Zur Chemie des Platins." Pt.  
Ann. Chem. (Liebig), 18 (1836), 105.
- 1836: 16. J. PELOUZE. Note sur la fabrication du platine. Pt.  
C. R. 3 (1836), 421; Ann. chim. phys. 62 (1836), 443; J. Frank. Inst. [2], 20 (1837), 53; Polyt. J. (Dingler), 63 (1837), 281.
- 1836: 17. J. VON LIEBIG. (Short note on preparation of platinum.)  
J. chim. méd. [2], 2 (1836), 581. Pt.
- 1836: 18. J. VON LIEBIG. (Malleable platinum.) Pt.  
Ann. chim. phys. 62 (1836), 443; Ann. des Mines [3], 11 (1837), 276.
- 1836: 19. C. S. M. POUILLET. Recherches sur les hautes températures. (Specific heat of platinum from 100° to 1200°.) Pt.  
C. R. 3 (1836), 782; Ann. der Phys. (Pogg.), 39 (1836), 571; Pharm. Centrbl. 1837, 274.
- 1836: 20. ————. (Alloys which may be substituted for platinum on lightning rods.) Pt.  
J. des connais. us. et pract. Sept. (1835); J. Frank. Inst. [2], 17 (1836), 427.
- 1837: 1. M. PETTENKOFER. (Very general occurrence of platinum, as in all silver coins.) Pt.  
Rep. für Pharm. (Buchner), 47 (1837), 72.
- 1837: 2. P. N. JOHNSON and W. A. LAMPADIUS. Ueber brasilianisches Palladgold und dessen Ausbringen und Scheidung. Pd.  
J. prakt. Chem. 10 (1837), 501; 11 (1837), 309; Ann. des Mines [3], 13 (1838), 713; Polyt. J. (Dingler), 68 (1838), 153; Phil. Mag. [3], 29 (1846), 130; J. Frank. Soc. [2], 19 (1837), 7; (from "Mining J."); Berzelius Jsb. 18 (1839), 145, 214.
- 1837: 3. G. F. C. FRICK. Ueber die Scheidung des Iridiums zum technischen Gebrauch im Grossen, aus den Rückständen von der Scheidung des Platins in Petersburg. Ir.  
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- 1837: 4. L. R. VON FELLEBERG. Neue Methode zur Auflösung des Iridiums—mit Berichtigung (by fusion with sulfur and alkaline carbonates). Ir.  
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- 1837: 5. R. W. BUNSEN. Notiz über die Schmelzbarkeit des Iridiums. (Mit Kohle vor dem Knallgebläse.) Ir.  
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- 1837: 6. J. F. SIMON. Beiträge zur Kenntniss des Arsens und seiner Verbindungen. (Arsenigsäures Platinoxyd-Ammoniak, p. 441.) Pt.  
Ann. der Phys. (Pogg.), 40 (1837), 411; Ann. Chem. (Liebig), 23 (1837), 271; Pharm. Centr. 1837, 410.
- 1837: 7. C. RAMMELSBURG. Ueber die einfachen und doppelten Cyanmetalle. (Platinum cyanids, p. 136; palladium cyanids, p. 137; iridium cyanids, p. 139.) Pt, Pd, Ir.  
Ann. der Phys. (Pogg.), 42 (1837), 111; Ann. Chem. (Liebig), 28 (1838), 216; Pharm. Centrbl. 1838, 39; Berzelius Jsb. 18 (1839), 163.
- 1837: 8. J. VON LIEBIG. Ueber die Aethertheorie, in besonderer Rücksicht auf die vorhergehende Abhandlung Zeise's (über entzündliches Platinchlorid). Pt.  
Ann. Chem. (Liebig), 23 (1837), 12; J. de Pharm. 24 (1838), 6; Berzelius Jsb. 18 (1839), 199.
- 1837: 9. G. J. MULDER. Over de eigenschappen en de zamenstelling van eenige Oenanthaten. (Platinum oenanthate.) Pt.  
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- 1837: 10. F. X. HAINDL. Ueber die Probe von platinhaltenden Gold- und Silberlegirungen. Pt.  
J. prakt. Chem. 10 (1837), 167.
- 1837: 11. R. BÖTTGER. Ueber Iridiumamalgam. Ir.  
J. prakt. Chem. 12 (1837), 352 (from Böttger, Beiträge zur Physik und Chemie, p. 103); Pharm. Centrbl. 1838, 26; Berzelius Jsb. 18 (1839), 149.

- 1838: 1. G. AIMÉ. Mineral de plomb sulfuré d'Alger. (Containing trace of platinum.) Pt.  
C. R. 7 (1838), 246.
- 1838: 2. A. DE LA RIVE. Sur l'oxidation du platine, et la théorie chimique de l'électricité voltaïque. Pt.  
C. R. 7 (1838), 1061; Ann. der Phys. (Pogg.), 46 (1839), 489; l'Institut 6 (1838), 414; Berzelius Jsb. 19 (1840), 141.
- 1838: 3. F. DÖBEREINER. Darstellung eines möglichst reinen Platinsalmiaks aus Platinerzlösung. Pt.  
Archiv der Pharm. 14 (1838), 274; Ann. Chem. (Liebig), 28 (1838), 238; Pharm. Centrbl. 1838, 602.
- 1838: 4. E. BIEWEND. Analyse des Rhodiumchloridnatriums, und über eine neue Rhodium-verbindung. (Aetherrhodiumchlorid-natrium.) Rh.  
J. prakt. Chem. 15 (1838), 126; Pharm. Centrbl. 1838, 925; Berzelius Jsb. 19 (1840), 268.
- 1838: 5. J. W. DÖBEREINER. Platinchlorid (resp. Platinoxid) und Schweflige Säure. Pt.  
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- 1838: 6. J. GROS. Recherches sur une série nouvelle de sels de platine. (Platinum-ammonium base.) Pt.  
Ann. chim. phys. 69 (1838), 204; Ann. Chem. (Liebig), 27 (1838), 241; Ann. des Mines [3], 15 (1839), 443; Årsb. phys. Kemi. 1839, 258; Pharm. Centrbl. 1838, 819; Phil. Mag. [3], 18 (1841), 284; Berzelius Jsb. 19 (1840), 269.
- 1838: 7. R. J. KANE. Ueber die Zusammensetzung einiger Quecksilberverbindungen und Ammoniakdoppelsalze. (Platin-ammonium compounds.) Pt.  
Ann. Chem. (Liebig), 26 (1838), 261.
- 1838: 8. W. C. ZEISE. Om Acechlorplatin, med bemaerkninger over nogle andre producter af virkningen mellem Platinchlorid og Acetone. Pt.  
Afhandl. Danske Vid. Selsk. [4], 8 (1841), 171; Oversigt. Danske Vid. Selsk. 1838, 3; 1839, 11; Ann. chim. phys. 72 (1839), 113; Ann. der Phys. (Pogg.), 45 (1838), 332; 47 (1839), 478; Ergänzt. bd. 2 (1842), 155, 312; J. prakt. Chem. 20 (1840), 193; Ann. Chem. (Liebig), 33 (1840), 29; Pharm. Centr. 1839, 43; 1840, 66, 81; Phil. Mag. [3], 14 (1839), 84; Ann. of Electric. (Sturgeon), 3 (1839), 488; Berzelius Jsb. 19 (1840), 603; 20 (1841), 88, 521.

- 1838: 9. W. H. ELLET. New mode of obtaining osmium. Os.  
J. Frank. Inst. [2], 21 (1838), 384.
- 1838: 10. H. REINSCH. Ueber das Fällungsverhältniss der wichtigern Metalle gegen Schwefelwasserstoffgas aus ihren mit Hydrochloresäure angesäuerten Lösungen. (Platin, p. 132.) Pt.  
J. prakt. Chem. 13 (1838), 132.
- 1838: 11. J. L. LASSAIGNE. Sur l'essai des soudes iodurées. (Use of palladium salts for the determination of iodine in varec soda.) Pd.  
J. chim. méd. [2], 4 (1838), 349; Pharm. Centrbl. 1839, 80.
- 1838: 12. R. HARE. Notice respecting the fusion of platina. Pt.  
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- 1838: 13. C. F. SCHÖNBEIN. Einige Bemerkungen über die Erfahrungen Hartley's in Betreff des Eisens (Platin-Eisen Legirung, p. 17). Pt.  
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- 1839: 2. L. HORNER. Verslag van een geologisch onderzoek van het zuid-oostelijke gedeelte van Borneo. (Occurrence and working of platinum, p. 111 and following.) Pt.  
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- 1840: 3. L. R. VON FELLENBERG. Ueber die Zersetzung der Schwefelmetalle durch Chlorgas. (Rhodium sulfid, p. 63; palladium sulfid, p. 65; iridium sulfid, p. 66; platinum sulfid, p. 70.) Pt, Pd, Rh, Ir.  
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palladium and platinum. (Palladium oxid, p. 276; chlorids, 280;  
sulfates, 287; nitrates, 292; oxalates, 297; platinum chlorid, 298;  
platinammonium compounds, 299.) Pt, Pd.  
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- 1842: 11. C. HIMLY. Vorläufige Notiz einer neuen Methode, die  
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potassium platinichlorid, p. 152.) Pt.  
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- 1842: 12. R. W. BUNSEN. On a new class of cacodyl compounds con-  
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- 1842: 17. R. HARE. [Fusion of platinum and iridium.] Pt, Ir.  
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Ann. Chem. (Liebig), 46 (1843), 182.
- 1843: 10. R. BÖTTGER. Warum versagt Platinschwamm so oft seinen Dienst. Pt.  
Ann. Chem. (Liebig), 47 (1843), 348; J. prakt. Chem. 30 (1843), 272; Ann. des Mines [4], 5 (1844), 445.
- 1843: 11. J. W. DÖBEREINER. Depotenzirende Wirkung des Ammoniaks auf zündenden Platinschwamm. Pt.  
J. prakt. Chem. 28 (1843), 165; Berzelius Jsb. 24 (1845), 147.
- 1843: 12. J. W. DÖBEREINER. Ueber Glycerin und Mannit. (Einwirkung von Platinschwamm.) Pt.  
J. prakt. Chem. 29 (1843), 451.
- 1843: 13. J. REISET and E. MILLON. Mémoire sur les phénomènes chimiques dûs au contact. (Action of platinum sponge on organic substances at high temperatures.) Pt.  
C. R. 16 (1843), 1190; Ann. chim. phys. [3], 8 (1843), 280; Ann. Chem. (Liebig), 48 (1843), 199; Bibl. Univ. 46 (1843), 169; J. prakt. Chem. 29 (1843), 365; l'Institut, No. 493; Pharm. Centrbl. 1843, 525; Berzelius Jsb. 24 (1845), 29.
- 1843: 14. C. F. SCHÖNBEIN. Einige Beobachtungen und Bemerkungen über den Einfluss, den gewisse Gasarten auf die Zündkraft des Platins ausüben. Pt.  
J. prakt. Chem. 29 (1843), 238; Bibl. Univ. 46 (1843), 113; Berzelius Jsb. 24 (1845), 147.
- 1843: 15. R. BÖTTGER. Ueber das Verplatiniren auf galvanischem Wege. Pt.  
J. prakt. Chem. 30 (1843), 267; Ann. Chem. (Liebig), 47 (1843), 342.
- 1843: 16. ———. Covering copper and brass with platinum. Pt.  
Ann. of Chym. and Pract. Pharm. 1843; J. Frank. Inst. [3], 6 (1843), 357.
- 1844: 1. M. LEPLAY. Recherches géologiques dans l'Oural. (Occurrence of platinum.) Pt.  
C. R. 19 (1844), 853.

- 1844: 2. M. M. KOSITZKY. Notiz über das uralsche Platin. (Composition of ore.) Pt.  
Verhandl. Min. Gesell. St. Petersburg. 1844, 165.
- 1844: 3. M. M. KOSITZKY. Ueber die Scheidung des Iridiums am Münzhofe zu St. Petersburg. Ir, Pt, Pd, Rh, Os.  
Verhandl. Min. Gesell. St. Petersburg. 1844, 178.
- 1844: 4. C. CLAUS. Untersuchung des Platinrückstandes, nebst vorläufiger Ankündigung eines neuen Metalles (Ruthenium). (Atomic weight of Ru = 104.57.) Pt, Pd, Ir, Os, Rh, Ru.  
Bul. Acad. Sci. St. Pétersb. 3 (1845), 38, 311, 354; Ann. Chem. (Liebig), 56 (1845), 257; J. prakt. Chem. 32 (1844), 479; 34 (1845), 173, 420; Ann. der Phys. (Pogg.), 64 (1845), 192; 65 (1845), 200; Ann. des Mines [4], 8 (1845), 234; Amer. J. Sci. 48 (1845), 401; Berzelius Jsb. 25 (1846), 205, 297; Pharm. Centrbl. 1844, 641, 646, 858; 1845, 353; Chem. Gaz. 3 (1845), Feb. 1; J. de Pharm. 7 (1845), 442; 8 (1845), 381; Phil. Mag. [3], 27 (1845), 230; Bibl. Univ. 58 (1845), 387; Oefversigt. Akad. Förh. Stockholm, 2 (1845), 1; 3 (1846), 61.
- 1844: 5. C. CLAUS. [Title in Russian.] (Chemical investigation of the residues of Uralian platinum and of the new metal ruthenium, Kazan, 1844. Demidoff Prize Essay.) Pt, Pd, Ir, Os, Rh, Ru.
- 1844: 6. C. CLAUS. (Fällung der Rhodiumlösung durch Kalk und durch borsaures Natron.) Rh.  
Bul. Acad. Sci. St. Pétersb. 2 (1843), 158.
- 1844: 7. E. FRÉMY. Recherches sur les acides métalliques. (Osmic acid.) Os, Ir.  
C. R. 18 (1844), 144; Ann. chim. phys. [3], 12 (1844), 457; Ann. des Mines [4], 5 (1844), 448; Ann. Chem. (Liebig), 52 (1844), 271; Amer. J. Sci. 48 (1845), 185; 49, 199; Berzelius Jsb. 25 (1845), 203, 232; J. de Pharm. 5 (1844), 188; J. prakt. Chem. 31 (1844), 482; 34 (1845), 303; Pharm. Centrbl. 1844, 266; 1845, 173; Polyt. J. (Dingler), 92 (1844), 208; Phil. Mag. [3], 24 (1844), 393, 474; Revue scient. 3 (1844), 333.
- 1844: 8. E. FRÉMY. Mémoire sur l'osmium. (Very full, including atomic weight Os = 199.65.) Os.  
C. R. 19 (1844), 468; J. de Pharm. 6 (1844), 241; J. prakt. Chem. 33 (1844), 407.
- 1844: 9. L. SCHAFFNER. Ueber die Zusammensetzung einiger Hydrate. Pt.  
Ann. Chem. (Liebig), 51 (1844), 168; Pharm. Centrbl. 1844, 913.

- 1844: 10. T. WERTHEIM. Untersuchung des Knoblauchöls. (Platinum and palladium compounds.) Pt, Pd.  
Ann. Chem. (Liebig), 51 (1844), 289; J. de Pharm. 7 (1845), 174; Berzelius Jsb. 25 (1846), 639.
- 1844: 11. M. PEYRONE. De l'action de l'ammoniaque sur le protochlorure de platine. Pt.  
Ann. chim. phys. [3], 12 (1844), 193; 16 (1846), 462; Ann. Chem. (Liebig), 51 (1844), 1; 55 (1845), 205; J. de Pharm. 9 (1846), 158; 12 (1847), 221; Pharm. Centrbl. 1844, 769, 784; 1846, 199; Berzelius Jsb. 25 (1846), 215, 242; 26 (1847), 264.
- 1844: 12. J. REISET. Mémoire sur les combinaisons de deux nouvelles bases alcalines contenant du platine. (Reiset's plat-ammonium base.) Pt.  
Ann. chim. phys. [3], 11 (1844), 417; J. prakt. Chem. 33 (1844), 321; Ann. Chem. (Liebig), 52 (1844), 262; Ann. des Mines [4], 8 (1845), 228; C. R. 18 (1844), 1100; Pharm. Centrbl. 1845, 113; Berzelius Jsb. 25 (1846), 214, 234.
- 1844: 13. J. BLYTH. On the composition of narcotine, and some of its products of decomposition by the action of bichloride of platinum. Pt.  
Proc. Chem. Soc. London, 2 (1844), 163; Ann. Chem. (Liebig), 50 (1844), 29; Phil. Mag. [3], 25 (1844), 363.
- 1844: 14. R. F. MARCHAND. Ueber das specifische Gewicht der Platina. J. prakt. Chem. 33 (1844), 385; Pharm. Centrbl. 1845, 191. Pt.
- 1844: 15. F. REICH. Notiz über das Kohlenoxydgasgebläse (Schmelzen des Platins). Pt.  
J. prakt. Chem. 33 (1844), 478.
- 1844: 16. A. PLEISCHL. Ueber das Entstehen der Blasen in Platin-geräthschaften. Pt.  
Ann. der Phys. (Pogg.), 63 (1844), 111; Pharm. Centrbl. 1845, 143.
- 1844: 17. J. W. DÖBEREINER. Erhöhung der oxydirenden Eigenschaften des Platinmohrs. Pt.  
J. für prakt. Pharm. 9 (1844), 233; Pharm. Centrbl. 1844, 879; Berzelius Jsb. 25 (1846), 213.
- 1844: 18. K. A. HIRSCHBERG. Ueber Anfertigung der Platinschwämmchen. Pt.  
Berliner Gew., Indust.- und Handelsblatt, 1, 2, No. 20; Polyt. J. (Dingler), 94 (1844), 208.
- 1844: 19. J. C. POGGENDORFF. Beschreibung der Wippe. (Action of platinized platinum plates.) Pt.  
Ann. der Phys. (Pogg.), 61 (1844), 593.

- 1844: 20. C. F. SCHÖNBEIN. Ueber den Einfluss, den gewisse Gasarten auf die Zündkraft des Platins ausüben. Pt.  
Ber. Verh. Naturf. Gesell. Basel, 6 (1844), 5.
- 1844: 21. G. WERTHEIM. Recherches sur l'élasticité. (Elasticity of platinum and palladium.) Pt, Pd.  
C. R. 19 (1844), 229; Ann. chim. phys. [3], 12 (1844), 385; Ann. der Phys. (Pogg.), Ergänz. bd. 2 (1848), 1.
- 1845: 1. E. L. SCHUBARTH. Ueber die vermeintliche Kenntniss der Alten von Platin. Pt.  
Ann. der Phys. (Pogg.), 65 (1845), 621.
- 1845: 2. J. S. C. SCHWEIGGER. Ueber Platina, altes und neues. (History of platinum.) Pt.  
J. prakt. Chem. 34 (1845), 385.
- 1845: 3. J. A. Ueber den Platingewinn in Russland. Pt.  
Allgemein. preuss. Ztg. ; Berg und Hütten Ztg. 4 (1845), 956, 975.
- 1845: 4. ———. Gold- und Platinaausbeute am Ural. Pt, &c.  
Bergwerksfreund, 9, Nr. 6; Pharm. Centrbl. 1845, 751.
- 1845: 5. C. CLAUS. Ueber die neuen Metalle, welche von Prof. Osann in dem Platinrückstande aufgefunden worden sind. (Polin, ruthenium and pluran.) Plu, Po, Ru, Os, Ir, Rh, Pt, Pd.  
Bull. Acad. Sci. St. Pétersb. 5 (1847), 182; J. prakt. Chem. 38 (1846), 164; Edinb. N. Phil. J. 39 (1845), 199.
- 1845: 6. G. OSANN. Bemerkungen über den Aufsatz des Herrn Prof. Claus, die von mir aufgefundenen neuen Metalle in dem Rückstande des uralschen Platins betreffend. (In J. prakt. Chem. 38, 164.) Ru, Plu, Po.  
Ann. der Phys. (Pogg.), 64 (1845), 208; J. prakt. Chem. 39 (1846), 111; Pharm. Centrbl. 1847, 74.
- 1845: 7. G. OSANN. Analyse des in Salpeter-Salzsäure unauflöslchen Rückstands des uralschen Platins. Plu, Po, Ru, Os, Ir, Rh, Pt, Pd.  
Ann. der Phys. (Pogg.), 64 (1845), 197; 69 (1846), 453; Pharm. Centrbl. 1847, 167.
- 1845: 8. C. CLAUS. Ueber das Polin des Herrn Prof. Osann.  
Ru, Po, Plu, Os, Ir, Rh, Pt, Pd.  
Ann. der Phys. (Pogg.), 64 (1845), 622.
- 1845: 9. [E. FRÉMY.] (Claim of priority on Claus' work on platinum residues.) Os.  
J. de Pharm. 8 (1845), 381; Phil. Mag. [3], 27 (1845), 233.



- 1845: 10. G. G. AQUILINA. Mémoire sur l'iode et sur un nouveau réactif de ce corps. (Iodic acid as a reagent for platinum.) Pt.  
J. chim. méd. [3], 1 (1845), 682. (Read before Soc. méd. d'encourag. de Malthe, Feb. 20, 1845.)
- 1845: 11. E. COTTEREAU, FILS. Note sur la valeur relative de l'amidon et du chlorure platinique employée comme réactifs de l'iode et des composés d'iode. Pt.  
J. chim. méd. [3], 1 (1845), 637; Pharm. Centrbl. 1846, 63.
- 1845: 12. H. KOPP. Specifisches Volum und specifisches Gewicht-Tabellen. Pt, Pd, Ir, Os, Rh.  
J. prakt. Chem. 34 (1845), 5.
- 1845: 13. L. ELSNER. Ueber die Trennung des Goldes und Platins von Zinn und Arsenik. Pt.  
J. prakt. Chem. 35 (1845), 310; Polyt. J. (Dingler), 98 (1845), 128; Pharm. Centrbl. 1845, 895; Berg und Hütten Ztg. 4 (1845), 1128.
- 1845: 14. K. W. G. KASTNER. Frei erhalten der Platin-Tiegel, -Bleche, -Löffel, -Spatel, und dergleichen vom Beitritt des Silic und des Eisens. (Protected in a Hessian crucible filled with calcium carbonate.) Pt.  
Arch. der Pharm. 94 (1845), 1; Pharm. Centrbl. 1845, 800.
- 1845: 15. J. WEIGER. (Preparation of alloys containing platinum and palladium for dentists.) (Alloys of platinum, gold, silver, and palladium.) Pt, Pd.  
London Journ. of Arts, 26 (1845), 398; Polyt. J. (Dingler), 97 (1845), 380.
- 1845: 16. J. W. DOBEREINER. Neue Beiträge zur Geschichte der chemischen Dynamik des Platins. (Platinum sponge.) Pt.  
Ann. der Phys. (Pogg.), 64 (1845), 94; Ann. Chem. (Liebig), 53 (1845), 145; J. de Pharm. 7 (1845), 356; Amer. J. of Sci. [2], 1 (1846), 110; Pharm. Centrbl. 1845, 350; Berzelius Jsb. 26 (1847), 179.
- 1845: 17. C. F. SCHÖNBEIN. On some chemical effects produced by platinum. (Platinum sponge on guaiacum, potassium iodid, potassium ferrocyanid.) Pt.  
Proc. Chem. Soc. London, 3 (1845), 17; Ann. der Phys. (Pogg.), 67 (1846), 233; Phil. Mag. 29 (1846), 40.
- 1845: 18. A. SCHROTTER. Modifications apportées à certaines reactions chimiques par une très-basse température. (Platinum sponge without effect on knallgas.) Pt.  
C. R. 20 (1845), 193; Ann. der Phys. (Pogg.), 64 (1845), 471.

- 1845: 19. P. RIESS. Ueber das Glühen und Schmelzen von Metall-  
drähten durch Elektricität. Pt.  
Abh. Acad. Berlin, 1845, 89; Ber. Acad. Berlin, 1845, 185; Ann.  
der Phys. (Pogg.), 65 (1845), 481; Scientif. Mem. (Taylor), 4  
(1846), 432; Berzelius Jsb. 26 (1847), 1.
- 1845: 20. N. W. FISCHER. Ueber das Vermögen mehrerer gas- und  
dunst-förmige Körper zu polarisiren und auf Iodkalium, Cyan-  
eisenkalium, etc., zersetzend einzuwirken. Pt.  
J. prakt. Chem. 34 (1845), 186; Berzelius Jsb. 26 (1847), 8.
- 1845: 21. J. C. POGGENDORFF. [Galvanische Reihe in Cyankalium-  
lösung.] Pt, Pd.  
Ann. der Phys. (Pogg.), 66 (1845), 597; Berzelius Jsb. 26 (1847), 12.
- 1846: 1. R. I. MURCHISON. Platinum of the Ural and Siberia. Pt.  
Amer. J. of Sci. [2], 2 (1846), 120; from "Russia and the Ural."
- 1846: 2. J. FRITZSCHE. Ueber eine vortheilhafte Methode der Auf-  
schliessung des Osmium-Iridiums. Os, Ir, Pt, Pd, Rh, Ru.  
Bull. Acad. Sci. St. Pétersb. 5 (1847), 186; J. prakt. Chem. 37  
(1846), 483; J. de Pharm. 1846, Sept.; Phil. Mag. [3], 29 (1846),  
420; Polyt. J. (Dingler), 103 (1847), 155; Ztsch. anal. Chem. 5  
(1866), 119; Pharm. Centrbl. 1846, 511; Berzelius Jsb. 27 (1848),  
129.
- 1846: 3. SCHMIDT and JOHNSTON. Sur le traitement du palladium. Pd.  
C. R. 22 (1846), 335; Ann. des Mines [4], 11 (1847), 525; l'Institut,  
No. 634, 65; Polyt. J. (Dingler), 99 (1846), 482; Berg u. Hütten  
Ztg. 5 (1846), 793; Chem. tech. Mitth. (Elsner), 1 (1846-48), 34.
- 1846: 4. G. OSANN. Platin im oxydirten Zustande. Pt.  
Ann. der Phys. (Pogg.), 67 (1846), 374; Pharm. Centrbl. 1846, 591.
- 1846: 5. W. KNOP and G. H. E. SCHNEIDERMAN. Ueber die Cyanver-  
bindungen des Platins. Pt.  
J. prakt. Chem. 37 (1846), 461; Ann. Chem. (Liebig), 64 (1847),  
300; J. de Pharm. 10 (1846), 223; Pharm. Centrbl. 1846, 633;  
Berzelius Jsb. 27 (1848), 192.
- 1846: 6. W. HAIDINGER. Merkwürdige Farbenvertheilung am Cyan-  
platinmagnesium. Pt.  
Haidinger Ber. 1 (1846), 3; Ann. der Phys. (Pogg.), 68 (1846), 302.
- 1846: 7. C. CLAUS. Ueber die chemischen Verhältnisse des Ruthen-  
iums, verglichen mit denen des Iridiums. Ru, Ir.  
Bull. Acad. Sci. St. Pétersb. 5 (1847), 241; Ann. Chem. (Liebig),  
59 (1846), 234; Ann. des Mines [4], 11 (1847), 526; J. prakt.  
Chem. 39 (1846), 88; J. de Pharm. 11 (1847), 76, 137; Phil. Mag.  
[3], 29 (1846), 556; Pharm. Centrbl. 1846, 817; Berzelius Jsb.  
27 (1848), 116 (with criticism by Berzelius), 132.

- 1846: 8. C. CLAUS. Test for ruthenium. (Fusion with salpeter and potash.) Ru.  
The Chemist, 1846, Jan. 1; Amer. J. of Sci. [2], 2 (1846), 111.
- 1846: 9. L. F. SVANBERG. (Osmic acid.) Os.  
Oefversigt. Akad. Förhand. 3 (1846), 36; Berzelius Jsb. 26 (1847), 181.
- 1846: 10. J. FRITZSCHE and H. STRUVE. Ueber die Osman-osmium-säure. Os.  
Bul. Acad. Sci. St. Pétersb. 6 (1848), 81; Ann. Chem. (Liebig), 64 (1847), 263; Ann. des Mines [4], 15 (1849), 149; J. de Pharm. [3], 12 (1847), 304 (with Gerhardt's comments); J. prakt. Chem. 41 (1847), 97; Phil. Mag. [3], 31 (1847), 534; Pharm. Centrbl. 1847, 385; Jsb. Chem. 1847-48, 461; Rapp. Ann. (Berzelius), 1847, 92; l'Institut, 17 (1849), 143; Berzelius Jsb. 27 (1848), 155.
- 1846: 11. RAEWSKY. Recherches sur les divers composés platiniques dérivés du sel vert de Magnus. Pt.  
C. R. 23 (1846), 353; 24 (1847), 1151; 25 (1847), 794; Ann. chim. phys. [3], 22 (1848), 278; J. de Pharm. [3], 12 (1847), 223; 14 (1848), 315 (with Gerhardt's comments); Ann. Chem. (Liebig), 64 (1847), 309; 68 (1848), 316; Pharm. Centrbl. 1847, 636; 1848, 109; Jsb. Chem. 1847-48, 455; J. Chem. Soc. 1 (1848), 189; Berzelius Jsb. 28 (1849), 158.
- 1846: 12. H. ROSE. Ueber die Einwirkung des Wassers auf Chlor-metalle. Pt, Pd.  
Ber. Acad. (Berlin), 1846, 186; Ann. der Phys. (Pogg.), 68 (1846), 444, 445; J. prakt. Chem. 38 (1846), 498.
- 1846: 13. C. R. FRESENIUS. Ueber die Löslichkeitsverhältnisse von einigen bei der quantitativen Analyse als Bestimmungsformen, etc., dienenden Niederschlägen. (Solubility of ammonium and potassium platinichlorid in alcohol.) Pt.  
Ann. Chem. (Liebig), 59 (1846), 117; Pharm. Centrbl. 1847, 36.
- 1846: 14. L. CROSNIER. Sur l'action réciproque de quelques sulfures métalliques naturels, et des sels de platine. Pt.  
C. R. 23 (1846), 217.
- 1846: 15. R. HARE. Fusion of iridium and rhodium. Ir, Rh.  
Amer. J. of Sci. [2], 2 (1846), 365; Rev. scient. 9 (1846), 233; Pharm. Centrbl. 1847, 415; Berzelius Jsb. 28 (1849), 76.
- 1846: 16. L. ELSNER. Beobachtungen über das Verhalten regulinischer Metalle in einer wässrigen Lösung von Cyankalium. (Platinum not soluble when used as anode.) Pt.  
J. prakt. Chem. 37 (1846), 441; Polyt. J. (Dingler), 101 (1846), 117; Pharm. Centrbl. 1846, 652; Berzelius Jsb. 27 (1848), 8.

- 1846: 17. L. PLAYFAIR and J. P. JOULE. Researches on atomic volumes and specific gravity. (Pt, Pd, Rh, Os, Ir, pp. 62, 63; Pt sponge, 69; Pt, 72; PtS, PdS, 89; allotropic conditions of Ir, Os, 97; Pt, 98.) Pt, Pd, Rh, Ir, Os.  
Proc. Chem. Soc. London, 3 (1846), 57; Phil. Mag. 27 (1845), 474.
- 1846: 18. TONNELIER. Einfaches Verfahren, chemische Gefässe von Gyps zu reinigen. (Boiling with solution of potassium carbonate.) Pt.  
Pharm. Centrbl. 1846, 271.
- 1846: 19. M. FARADAY. Magnetism and diamagnetism of metals. Pt, Pd, Rh, Ir, Os.  
Phil. Trans. London, 136 (1846), 47; Ann. der Phys. (Pogg.), 70 (1847), 35; Bibl. Univ. Arch. 2 (1846), 145.
- 1846: 20. C. F. SCHÖNBEIN. On the influence exerted by electricity, platinum, and silver upon the luminosity of phosphorus. Pt.  
Proc. Chem. Soc. Lond. 3 (1846), 104; Ann. der Phys. (Pogg.), 68 (1846), 37; Phil. Mag. [3], 29 (1846), 122.
- 1846: 21. E. BECQUEREL. Recherches sur la conductibilité électrique des corps solides et liquides. (Conductivity of platinum and palladium.) Pt, Pd.  
C. R. 22 (1846), 416; Ann. chim. phys. [3], 17 (1846), 242; Ann. der Phys. (Pogg.), 70 (1847), 243; Amer. J. Sci. 8 (1849), 185; Jsb. Chem. 1847-48, 289.
- 1846: 22. W. R. GROVE. On certain phenomena of voltaic ignition, and the decomposition of water into its constituent gases by heat. (Decomposition by platinum and osmiridium.) Bakerian Lecture. Pt, Os, Ir.  
Phil. Trans. London, 137 (1847), 1, 17; Proc. Roy. Soc. London, 3 (1851), 657; Phil. Mag. [3], 31 (1847), 20, 91, 96; Ann. chim. phys. 21 (1847), 129; Bibl. Univ. Arch. 5 (1847), 18, 112; J. prakt. Chem. 43 (1848), 309; J. de Pharm. 12 (1847), 154; 14 (1848), 29; Ann. Chem. (Liebig), 63 (1847), 1; Ann. der Phys. (Pogg.), 71 (1847), 194; Pharm. Centrbl. 1847, 632.
- 1847: 1. MAXIMILIAN HERZOG VON LEUCHTENBERG. Weitere Untersuchungen des schwarzen Niederschlages, welcher sich an der Anode bei der Zersetzung des Kupfervitriols durch den galvanischen Strom bildet. (Platinum in copper ores.) Pt.  
Bull. Acad. Sci. St. Pétersb. 6 (1848), 129; J. prakt. Chem. 41 (1847), 222; Polyt. J. (Dingler), 106 (1847), 35; Jsb. Chem. 1847-48, 1022; Berzelius Jsb. 28 (1849), 85.
- 1847: 2. MOLNÁR. (Platinum in sand from Ohlápian, Hungary.) Pt.  
Haidinger Ber. 3 (1847), 412, 475; Jsb. Chem. 1847-48, 1152.

- 1847: 3. KOPETZKY and A. PATERA. (Platinum not in Ohlápian sand.)  
Haidinger Ber. 3 (1847), 439; Jsb. Chem. 1847-48, 1152. Pt.
- 1847: 4. C. U. SHEPARD. Native platinum in North Carolina. (Rutherford Co.) (Mistake, see 1892: 1.) Pt.  
Amer. J. Sci. [2], 4 (1847), 280; Ann. der Phys. (Pogg.), 74 (1848), 320; J. prakt. Chem. 45 (1848), 454; Pharm. Centrbl. 1848, 511; Jsb. 1847-48, 1152; Berg und Hütten Ztg. 8 (1849), 79.
- 1847: 4½. QUINTUS ICILIUS. Die Atomgewichte vom Palladium, Kalium, Chlor, Silber, Kohlenstoff, und Wasserstoff, nach der Methode der kleinsten Quadrate berechnet. Inaug. Diss. Göttingen, 1847. (Pd = 111.879.) Pd.
- 1847: 5. M. PETTENKOFER. Ueber die Affinirung des Goldes und über die grosse Verbreitung des Platins. Pt.  
Gelehrte Anz. München, 24 (1847), 589; Bull. Akad. Sci. München, 1847, 101; Polyt. J. (Dingler), 104 (1847), 118, 198; Ann. Chem. (Liebig), 64 (1847), 294; Repert. der Pharm. 1847, 72; Pharm. Centrbl. 1847, 766; Berzelius Jsb. 28 (1849), 85.
- 1847: 6. H. HESS. Note sur le traitement du mineral de platine. (Fusion with zinc.) Pt, Pd, Rh, Ir, Os, Ru.  
Bull. Acad. Sci. St. Pétersb. 6 (1848), 80; Ann. Chem. (Liebig), 64 (1847), 267; Ann. des Mines [4], 15 (1849), 149; 19 (1851), 415; l'Institut, 17 (1849), 144; J. prakt. Chem. 40 (1847), 498; Polyt. J. (Dingler), 104 (1847), 468; J. Frank. Inst. [3], 15 (1848), 388; Jsb. Chem. 1847-48, 453; Civ. Eng. and Arch. Journ. ; Chem. tech. Mitth. (Elsner), 1 (1846-48), 48; Berzelius Jsb. 28 (1849), 85.
- 1847: 7. C. CLAUS. Beiträge zur Chemie der Platinmetalle. (Iridiumchlorid, and sulfites, p. 273; osmium sulfites, 278; platinum sulfites, 287; ruthenium sulfites, 288.) Pt, Pd, Rh, Ir, Os, Rh.  
Bull. Acad. Sci. St. Pétersb. 6 (1848), 273; Ann. Chem. (Liebig), 63 (1847), 337; J. prakt. Chem. 42 (1847), 348; J. de Pharm. [3], 14 (1848), 385; Pharm. Centrbl. 1847, 849, 867; Jsb. Chem. 1847-48, 453, 457, 458, 461; l'Institut, 17 (1849), 143, 244; Ann. des Mines [4], 19 (1851), 415; Phil. Mag. [3], 35 (1849), 396; Amer. J. Sci. [2], 9 (1850), 422; Berzelius Jsb. 28 (1849), 76.
- 1847: 8. C. CLAUS. [Iridiumchlorid.] Ir.  
Berzelius Jsb. 26 (1847), 262.
- 1847: 9. C. CLAUS. [Verhalten des Iridiums gegen schmelzendes Kali und Salpeter.] Ir.  
Berzelius Jsb. 26 (1847), 184.
- 1847: 10. C. CLAUS (J. J. BERZELIUS). [Vorkommen des Rutheniums, Methode auszuziehen, und Beschreibung der Salze.] (This

contains Berzelius' criticism of Claus' discovery that the  $3\text{KCl}, \text{IrCl}_3$  of Berzelius is really  $2\text{KCl}, \text{RuCl}_4$ —in reality it is  $2\text{KCl}, \text{RuCl}_3\text{NO}$ , see 1889: 9 and 1894: 11.) Ru, Ir.

Berzelius Jsb. 26 (1847), 181.

- 1847: 11. N. W. FISCHER. Zur Geschichte des Palladiums. (Verhalt zu Säuren, Pogg. 71: 432; zu Alkalien, 437; Doppelsalze, 440.) Pd.

Uebers. Schles. Gesell. Breslau, 1847, 30; Ann. der Phys. (Pogg.), 71 (1847), 431; Ann. Chem. (Liebig), 64 (1847), 260; Pharm. Centrbl. 1847, 554; Jsb. Chem. 1847-48, 457; Berzelius Jsb. 28 (1849), 86.

- 1847: 12. C. CLAUS. [Platin Ammoniak: Neue Basis aus einem Atome Platinoxid und zwei Aequivalente Ammoniak.] Pt.  
Berzelius Jsb. 26 (1847), 180.

- 1847: 13. M. PEYRONE. Recherche comparative sopra alcuni isomeri del sal verde di Magnus. Pt.  
Mem. Acad. Torino. 10 (1849), 171; Ann. Chem. (Liebig), 61 (1847), 178; Pharm. Centrbl. 1847, 411; Jsb. Chem. 1847-48, 454; Berzelius Jsb. 28 (1849), 154.

- 1847: 14. B. QUADRAT. Ueber Verbindungen des Platinecyanürs mit Cyanmetallen und über die Platinblausäure. Pt.  
Abhandl. Böhm. Gesell. [5], 5 (1847), 16; Sitzber. Akad. Wien. 3 (1849), 10; Ann. Chem. (Liebig), 63 (1847), 164; 65 (1848), 249; 70 (1849), 300; J. de Pharm. [3], 12 (1847), 457; Pharm. Centrbl. 1848, 97; 1849, 657; Jsb. Chem. 1847-48, 482; 1849, 301; Berzelius Jsb. 28 (1849), 147.

- 1847: 15. C. RAMMELSBERG. Ueber ein neues Kaliumkupfercyanur. (Mercury platinocyanid.) Pt.  
Ann. der Phys. (Pogg.), 73 (1848), 117; J. prakt. Chem. 41 (1847), 184; Ber. Acad. Berlin, 1847, 115; Jsb. Chem. 1847-48, 484.

- 1847: 16. A. LAURENT. Sur les polycyanures. (Important article on theory of double cyanids.) Pt.  
C. R. 26 (1848), 295; J. prakt. Chem. 42 (1847), 128; Pharm. Centrbl. 1848, 423; Jsb. Chem. 1847-48, 484.

- 1847: 17. W. HÄIDINGER. Ueber das Schillern der Krystallflächen. (Platinocyanids of magnesium, barium, and potassium, and platinum oxalate.) Pt.  
Haidinger, Ber. 2 (1847), 98; Haidinger Abhandl. 1 (1847), 143; Ann. der Phys. (Pogg.), 70 (1847), 574; 71 (1847), 321; Jsb. Chem. 1847-48, 195.

- 1847: 18. W. HÄIDINGER. Platinverbindungen mit schillernden Flächen. (Cyanids and oxalate.) Pt.  
Haidinger, Ber. 2 (1847), 198, 263.

- 1847: 19. W. HITTORF. Ueber die Bildung einer blauen Oxydationsstufe des Platins . . . auf galvanischem Wege. Pt.  
Ann. der Phys. (Pogg.), 72 (1847), 481; Ann. Chem. (Liebig), 64, (1847), 268; J. prakt. Chem. 42 (1847), 469; Pharm. Centrbl. 1848, 23; Jsb. Chem. 1847-48, 453; Berzelius Jsb. 28 (1849), 84.
- 1847: 20. L. KESSLER. Note sur l'emploi de l'acétate ferreux comme moyen de séparation de l'argent. (Precipitation of platinum by iron sulfate with acetic acid.) Pt.  
J. de Pharm. [3], 11 (1847), 86; Palomba, Raccolta, 3 (1847), 379; Pharm. Centrbl. 1847, 413.
- 1847: 21. R. HARE. On certain improvements in the construction and supply of the hydro-oxygen blowpipe, by which rhodium, iridium, or the osmiuret of iridium, also platinum in the large way, have been fused. Pt, Ir, Rh, Os.  
J. Frank. Inst. [3], 13 (1847), 196; Amer. J. Sci. [2], 4 (1847), 37; Phil. Mag. [3], 31 (1847), 147, 356; Polyt. J. (Dingler), 108 (1848), 270.
- 1847: 22. R. HARE. Apparatus for the fusion of iridium or rhodium, or masses of platinum less than five ounces in weight. Pt, Ir, Rh.  
J. Frank. Inst. [3], 14 [1847], 128.
- 1847: 23. H. H[ESS]. Schmelzbarkeit des Iridiums, des Osmiridiums und des Rhodiums. Pt, Ir, Os, Rh.  
Berg und Hütten Ztg. 6 (1847), 107.
- 1847: 24. F. LÜDERSDORFF. (Platinum on porcelain.) Pt.  
Verh. Gew. Bef. Preus. 1847, ii, 67; Polyt. J. (Dingler), 105 (1847), 36; Jsb. Chem. 1847-48, 1067; Chem. tech. Mitth. (Elsner), 1 (1846-48), 18.
- 1847: 25. MENTION and WAGNER. Platin als Legirung zu Schmucksachen, etc. Pt.  
Brevets d'Invention, 1847, 425; Polyt. Centrbl. 1848, Mar. 1; Polyt. J. (Dingler), 108 (1848), 396.
- 1847: 26. G. WILSON. On the decomposition of water by platinum and the black oxide of manganese at a white heat, with some observations on the theory of Mr. Grove's experiments. Pt.  
Proc. Chem. Soc. Lond. 3 (1847), 332; Trans. Scot. Soc. Arts, 3 (1851), 170; Edinb. N. Phil. J. 43 (1847), 244; Chem. Gaz. 5 (1847), 198; Phil. Mag. 31 (1847), 177.
- 1847: 27. J. LAMONT. Reduction der Schwingungen eines Magnets auf den luftleeren Raum. (Polarität des Palladiums und Platins.) Pt, Pd.  
Ann. der Phys. (Pogg.), 71 (1847), 128.

- 1848: 1. É. GUEYMARD. Mémoire historique sur la découverte du platine dans les Alpes. Pt.  
Moniteur Indust. 1848, Sept. 14; J. prakt. Chem. 45 (1848), 454; C. R. 29 (1849), 814; Ann. des Mines [4], 14 (1848), 331; 16 (1849), 495; Ann. der Phys. (Pogg.), 79 (1850), 480; Amer. J. Sci. [2], 7 (1849), 137; Phil. Mag. [3], 36 (1850), 323; Jsb. Chem. 1849, 726; Polyt. J. (Dingler), 115 (1850), 395; Berg und Hütten Ztg. 9 (1850), 479.
- 1848: 2. A. FABER. Producte Ostindiens. (Platinum in Burmah.) Pt.  
Pharm. Centrbl. 1848, 569.
- 1848: 3. M. PETTENKOFER. Ueber die grosse Verbreitung des Platins und sein Vorkommen in allen güldischen Silbermünzen. Pt.  
Bull. Akad. München, 1848, 142; Ann. der Phys. (Pogg.), 74 (1848), 316; Rep. für Pharm. (Buchner) [2], 47 (1847), 72; Revue scientifique, 5 (1849), 231; Jsb. Chem. 1847-48, 453.
- 1848: 4. C. F. PLATTNER. Untersuchung des Rückstandes von der Freiburger Silbererz-Amalgamation auf einen Gehalt an Gold und Platin. Pt.  
Berg und Hütten Ztg. 7 (1848), 628.
- 1848: 5. N. W. FISCHER. Ueber die salpetrichsauren Salze. (Salpetrichsaures Palladiumoxydkali.) Pd.  
Uebers. Schles. Gesel. Breslau, 1848, 31; Ann. der Phys. (Pogg.), 74 (1848), 123; J. prakt. Chem. 46 (1849), 318; Pharm. Centrbl. 1848, 401.
- 1848: 6. RAEWSKY. Mémoire sur les combinaisons du platine avec la nicotine. Pt.  
C. R. 27 (1848), 609; Ann. chim. phys. [3], 25 (1849), 332; J. prakt. Chem. 46 (1849), 470; Ann. Chem. (Liebig), 70 (1849), 232; Pharm. Centrbl. 1849, 329.
- 1848: 7. RAEWSKY. Recherches sur les sels anilicoplatiniques. Pt.  
C. R. 26 (1848), 424; Pharm. Centrbl. 1848, 400; Jsb. Chem. 1847-48, 655.
- 1848: 8. J. BLYTH. On the composition of coniine, and its products of decomposition. (Action of platinum chlorid.) Pt.  
Q. J. Chem. Soc. 1 (1848), 345; Ann. Chem. (Liebig), 70 (1849), 73.
- 1848: 9. F. M. BAUMERT. Analyse des Platincyanmagnesiumsalz des Quadrat's. Pt.  
Ann. Chem. (Liebig), 65 (1848), 250, foot-note; Jsb. Chem. 1847-48, 484.
- 1848: 10. LYONS and MILLWARD. Alloy of copper with platinum and palladium. Pt, Pd.  
Repert. Patent Invent. Feb. 1848, 114; Polyt. J. (Dingler), 108 (1848), 398.



- 1848: 11. G. OSANN. Ueber die Bestimmung specifischer Gewichte fester Körper. (Specific gravity of platinum.) Pt.  
Ann. der Phys. 73 (1848), 605; Pharm. Centrbl. 1848, 330; Jsb. Chem. 1847-48, 38.
- 1848: 12. G. ROSE. Nachträgliche Bemerkungen über das specifische Gewicht des pulverförmigen Platins. Pt.  
Ann. der Phys. (Pogg.), 73 (1848), 13; 75 (1848), 403; Ann. Chem. (Liebig), 68 (1848), 159; Pharm. Centrbl. 1848, 91; Jsb. Chem. 1847-48, 37.
- 1849: 1. J. J. EBELMEN. Rapport sur l'existence du platine dans certains minerais du département de l'Isère. Pt.  
Ann. des Mines [4], 16 (1849), 505.
- 1849: 2. ————. Platinum in California. Pt.  
Amer. J. Sci. [2], 8 (1849), 294; Edinb. N. Phil. J. 48 (1850), 185.
- 1849: 3. ————. Sur la production des mines d'or et de platine de l'Oural en 1849. Pt, Ir, Os.  
Ann. des Mines [4], 16 (1849), 531.
- 1849: 4. P. JEWREINOW. Ueber ein schwarzes Salz, das man bei Ausscheidung des Iridiums aus Platinrückständen erhält. (Potassium iridium chlorid.) Ir.  
Berg Journal (St. Pétersburg), 1849, Th. 1, Heft 3; Berg und Hütten Ztg. 12 (1853), 193.
- 1849: 5. A. SCHRÖTTER. Ueber die auf directem Wege darstellbaren Verbindungen des Phosphors mit den Metallen. (Union of phosphorus with platinum and palladium.) Pt, Pd, Ir.  
Sitzber. Acad. Wien. 2 (1849), 301.
- 1849: 6. A. LAURENT and C. GERHARDT. De l'action de l'ammoniaque sur le chloroplatinate d'ammoniaque. (Theory of platinum bases and double cyanids.) Pt.  
Laurent et Gernhardt, C. R. 1849, 113; 1850, 145; Ann. Chem. (Liebig), 73 (1850), 223; J. prakt. Chem. 46 (1849), 511; Chem. Centrbl. 1850, 437, 471; Jsb. Chem. 1849, 289; 1850, 360.
- 1849: 7. W. HÄIDINGER. Ueber die Formen und einige optische Eigenschaften der Magnesium-Platin-Cyanüre. Pt.  
Sitzber. Acad. Wien. 1849, 20; Ann. der Phys. (Pogg.), 77 (1849), 89; Jsb. Chem. 1849, 122.
- 1849: 8. F. BRAUELL. De acidi osmici in homines et animalia effectu. Casani, 1849. Os.

- 1849: 9. M. PETTENKOFER. Ueber die Bestandtheile der Schlacken, welche beim Schmelzen des Scheidegoldes mit Salpeter gebildet werden, und über deren Benutzung. Pt, Pd, Os.  
Polyt. J. (Dingler), 111 (1849), 357; Jsb. Chem. 1849, 635; Polyt. Centrbl. (1849), 926, 933.
- 1849: 10. G. ROSE. Ueber die Krystallform der rhomboëdrischen Metalle, namentlich des Wismuths. (Auch Palladiums, Iridiums und Osmiums.) Pd, Ir, Os.  
Abhandl. Acad. Berlin (Phys.), 1849, 72; Ber. Acad. Berlin, 1849, 137; Ann. Chem. (Liebig), 76 (1850), 245; Ann. der Phys. (Pogg.), 77 (1849), 149; J. prakt. Chem. 49 (1850), 163; Jbuch Min. 1849, 566; l'Institut, 1849, 342; Pharm. Centrbl. 1849, 489; Jsb. Chem. 1849, 13.
- 1849: 11. A. SALVÉTAT. Note sur un nouvel emploi du platine dans la peinture sur porcelaine. Pt.  
Ann. chim. phys. [3], 25 (1849), 342; Ann. Chem. (Liebig), 72 (1849), 263; Ann. des Mines [4], 19 (1851), 414; J. prakt. Chem. 47 (1849), 232; Pharm. Centrbl. 1849, 260; Polyt. J. (Dingler), 112 (1849), 45; Jsb. Chem. 1849, 652.
- 1849: 12. J. FIELD. On the chemical combinations induced in gaseous mixtures by contact with certain metals, with especial reference to the action of spongy platinum on mixtures of oxygen and hydrogen. (Cause.) Pt.  
Pharm. Journ. and Trans. 8 (1849), 381; Pharm. Centrbl. 1849, 381.
- 1849: 13. C. DESPRETZ. Sur la fusion et la volatilization des corps réfractaires. Note sur quelques expériences faites avec le triple concours de la pile voltaïque, du soleil, et du chalumeau. Pt, Pd.  
C. R. 29 (1849), 545; Ann. des Mines [4], 19 (1851), 333; l'Institut, 811, 226; 829, 368; Chem. Centrbl. 1850, 22.
- 1850: 1. C. DE PARAVEY. Sur quelques passages de Pline l'Ancien qui semblent pouvoir se rapporter au platine (livre 33 : 3 et 34 : 16). Pt.  
C. R. 31 (1850), 179.
- 1850: 2. W. MALLET. On the minerals of the auriferous districts of Wicklow. Pt.  
Journ. Geol. Soc. Dublin, 4 (1850), 269; Amer. J. Sci. [3], 11 (1851), 232; Phil. Mag. [3], 37 (1850), 393; Jsb. Chem. 1850, 699.
- 1850: 3. R. M. PATTERSON. Ueber die Beschaffenheit und das Vorkommen des Goldes, Platins und der Diamanten in den Vereinigten Staaten. Pt, Ir, Os.  
Ztsch. Deutsch. Geol. Gesell. 2 (1850), 60; Jahrbuch Min. 1851, 351; Jsb. Chem. 1850, 698; Berg und Hütten Ztg. 9 (1850), 609.

- 1850: 4. J. E. TESCHEMACHER. Platinum of California. Pt.  
Amer. J. Sci. [2], 10 (1850), 121; Edinb. N. Phil. J. 51 (1851), 193;  
Chem. Centrbl. 1851, 640; Jsb. Chem. 1850, 699.
- 1850: 5. T. THOMSON. Biographical account of Dr. Wollaston. (Ac-  
count of his discoveries.) Pt, Pd, Rh.  
Proc. Phil. Soc'y, Glasgow, 3 (1850), 129.
- 1850: 6. E. FREMY. Recherches chimique sur l'or. (Note on making  
platinates, Ann. chim. phys. 31 : 482.) Pt.  
C. R. 31 (1850), 893; Ann. chim. phys. [3], 31 (1851), 478; Ann.  
Chem. (Liebig), 79 (1851), 43; J. prakt. Chem. 52 (1851), 159;  
J. de Pharm. 19 (1851), 84.
- 1850: 7. C. A. WURTZ. Mémoire sur une série d'alcaloïdes homologues  
avec l'ammoniaque. (Platino- and platinichlorids of methyl-,  
ethyl-, and amyl-amin.) Pt.  
Ann. chim. phys. [3], 30 (1850), 443; J. prakt. Chem. 52 (1851),  
193; Chem. Centrbl. 1851, 166, 177; Jsb. Chem. 1850, 335, 443.
- 1850: 8. C. GERHARDT. Recherches sur les combinaisons ammoniacales  
du platine. Pt.  
Gerhardt et Laurent, C. R. 1850, 273; C. R. 31 (1850), 241; Ann.  
Chem. (Liebig), 76 (1850), 307; Ann. des Mines [4], 19 (1851),  
414; J. prakt. Chem. 51 (1850), 331; 53 (1851), 345; Chem. Centrbl.  
1851, 97.
- 1850: 9. J. SCHABUS. Ueber die Krystallformen des Barium-Platin-  
Cyanürs. Pt.  
Sitzber. Acad. Wien, 4 (1850), 569; Jsb. Chem. 1850, 360.
- 1850: 10. A. REYNOSO. De l'action des bases sur les sels, et en parti-  
culier sur les arsénites. (Reduction of palladium salts by silver  
arsenite.) Pd.  
C. R. 31 (1850) 68; Ann. chim. phys. [3], 33 (1851), 245; J. prakt.  
Chem. 51 (1850), 160; 54 (1851), 309.
- 1850: 11. A. MASSON. Études de photométrie électrique. (Spectre  
du platine incandescent.) Pt.  
C. R. 31 (1850), 887; 32 (1851), 127; Ann. chim. phys. [3], 31 (1851),  
323.
- 1850: 12. J. P. JOULE. On some amalgams. (Platinum amalgam,  
Pt Hg<sub>2</sub>.) Pt.  
Rept. Brit. Assoc. 1850, ii, 55; Chem. Gaz. 1850, 339; l'Institut, 1850,  
327; Jsb. Chem. 1850, 333.
- 1850: 13. A. BAUDRIMONT. Expériences sur la ténacité des métaux  
malléables. (Tenacity of palladium and platinum.) Pd, Pt.  
Ann. chim. phys. [3], 30 (1850), 304; C. R. 31 (1850), 115; Ann.  
Chem. (Liebig), 76 (1850), 123; Ann. der Phys. (Pogg.), 82

- (1851), 156; l'Institut, 18 (1850), 241; J. de Pharm. 19 (1851), 206; Phil. Mag. [3], 37 (1850), 308; Jsb. Chem. 1850, 78.
- 1850: 14. C. BROMEIS. Ueber das Plattiren mit Platinum. Pt.  
Polyt. J. (Dingler), 116 (1850), 283; Jsb. Chem. 1850, 631.
- 1850: 15. A. WAGNER. Ersatzmittel des Schwammplatin bei Wein-  
geistglühlampen. (Chromate of copper.) Pt.  
Polyt. Centrbl. 16 (1850), Nr. 1; Polyt. J. (Dingler), 115 (1850),  
159; Chem. Centrbl. 1850, 157.
- 1850: 16. D. BREWSTER. On the optical properties of the cyanurets of  
platinum and magnesia, and of barytes and platinum. Pt.  
Rept. Brit. Assoc. 1850, ii, 5.
- 1851: 1. T. S. HUNT. [Platinum and iridosmine in Canada.]  
Pt, Ir, Os.  
Report Geol. Surv. Canada, 1851-52, 120; Amer. J. Sci. [2], 15  
(1853), 448; Ann. des Mines [5], 3 (1853), 683.
- 1851: 2. F. A. GENTH. Nord-Amerikanische Mineralien. (Platinum  
from Lancaster Co., Pa.) Pt.  
Nord-Amer. Monatsber. 2 (1851), June; J. prakt. Chem. 55 (1852),  
254; Chem. Centrbl. 1851, 417; Berg u. Hütten Ztg. 11 (1852), 328.
- 1851: 3. G. A. KENNGOTT. Irite. Ir, Os.  
Amer. J. Sci. [2], 11 (1851), 232; from Mineral. Untersuchungen,  
1, 61.
- 1851: 4. J. J. EBELMAN. Sur la cristallisation par la voie sèche. (Arti-  
ficial octahedral crystals of platinum.) Pt.  
C. R. 32 (1851), 710; Ann. Chem. (Liebig), 80 (1851), 212.
- 1851: 5. F. CLAUDET. On a class of ammoniacal compounds of cobalt.  
(Platinum salts of cobaltamins.) Pt.  
Phil. Mag. [4], 2 (1851), 253; Ann. chim. phys. [3], 33 (1851), 483;  
J. prakt. Chem. 54 (1851), 270; Chem. Centrbl. 1851, 865; J. Chem.  
Soc. 4 (1851), 355.
- 1851: 6. H. H. LANDOLT. Ueber das Stibmethyl und seine Verbind-  
ungen. (Double chlorid of platinum and tetramethylstibonium.)  
Pt.  
Mitth. nat.forsch. Gesell. Zurich, 2 (1850-52), 349, 524; Ann. chim.  
phys. 34 (1852), 226; 37 (1853), 60; Ann. Chem. (Liebig), 78  
(1851), 91; 84 (1852), 44; J. prakt. Chem. 52 (1851), 385; 57 (1852),  
129; J. de Pharm. 20 (1851), 65; Chem. Centrbl. 1852, 625.
- 1851: 7. A. W. HOFMANN. Researches into the molecular constitution  
of the organic bases. II. (Platinum bases, p. 397.) Pt.  
Phil. Trans. London, 141 (1851), 357; Ann. chim. phys. [3], 33  
(1851), 108; Ann. Chem. (Liebig), 78 (1851), 253; 79, 11; C. R.

33 (1851), 95; l'Institut, 19 (1851), 189; J. de Pharm. [3], 20 (1851), 220; J. prakt. Chem. 53 (1851), 390; Laurent et Gerhardt, C. R. 1851, 189; Q. J. Chem. Soc. 4 (1852), 304; Chem. Centrbl. 1851, 772, 787; Jsb. Chem. 1851, 496.

- 1851: 8. G. B. BUCKTON. Observations upon the deportment of diplatosamine with cyanogen. Pt.  
Q. J. Chem. Soc. 4 (1851), 26; Ann. Chem. (Liebig), 78 (1851), 328; J. de Pharm. 19 (1851), 393; J. prakt. Chem. 53 (1851), 174; Laurent et Gerhardt, C. R. 1851, 91; Chem. Centrbl. 1851, 696; Jsb. Chem. 1851, 370; Ann. chim. phys. (1851), 393.
- 1851: 9. J. L. LASSAIGNE. Observations sur le degré de sensibilité des divers réactifs par l'iode, et ses divers composés. (Use of palladium salts.) Pd.  
J. chim. méd. [3], 7 (1851), 142; J. de Pharm. 19 (1851), 428.
- 1851: 10. A. BUTLEROW. Ueber die oxydirende Wirkung der Osmiumsäure auf organische Körper. Os.  
Bull. Acad. Sci. St. Pétersb. 10 (1852), 177; Ann. Chem. (Liebig), 84 (1852), 278; J. prakt. Chem. 56 (1852), 271; l'Institut, 20 (1852), 249; Jsb. Chem. 1852, 429; Mélanges phys. chim. Acad. St. Pétersb. 1 (1851), 355.
- 1851: 11. M. G. VON PAUCKER. Das astronomische Längenmaas. (Ausdehnung des Platins.) Pt.  
Bul. Acad. Sci. St. Pétersb. 10 (1852), 209; Jsb. Chem. 1852, 2.
- 1851: 12. A. BAUDRIMONT. Expériences sur l'élasticité des corps hétérophones. Pt.  
Ann. chim. phys. [3], 32 (1851), 288; Jour. für Physik. 2 (1851), 533; Jsb. Chem. 1851, 82.
- 1851: 13. A. C. BECQUEREL. Mémoire sur les effets électriques produits dans les tubercules, les racines et les fruits, lors de l'introduction d'aiguilles galvanométriques en platine. Pt.  
C. R. 32 (1851), 657; Mém. l'Institut, 23 (1853), 301.
- 1852: 1. É. GUEYMARD. Recherches analytiques du platine dans les Alpes. Pt.  
Ann. des Mines [5], 1 (1852), 345; 5 (1854), 165; C. R. 38 (1854), 941; 40 (1855), 1274; Arch. des sci. phys. nat. 27 (1854), 77; Bul. Géol. Soc. Paris, 12 (1854-55), 429; Jsb. Chem. 1852, 831; 1854, 807; 1855, 905; l'Institut, 23 (1855), 212; Chem. Centrbl. 1855, 543; Berg u. Hütten Ztg. 12 (1853), 752.
- 1852: 2. F. A. GENTH. On some minerals which accompany gold in California. (Platinum and osmiridium.) Pt, Ir, Os.  
Proc. Acad. Nat. Sci. Phila. 6 (1852), 113; Nord-Amer. Monatsber. 2 (1852), 205, 249; Ann. des Mines [5], 4 (1853), 130; Amer. J.

- Sci. [2], 14 (1852), 277; Edinb. N. Phil. J. 54 (1853), 182; J. prakt. Chem. 58 (1853), 245; Chem. Centrbl. 1852, 72; Jsb. Chem. 1852, 831; Berg u. Hütten Ztg. 12 (1853), 751.
- 1852: 3. F. A. GENTH. On a probably new element with iridosmine and platinum from California. Pt, Ir, Os, Pd, Rh, Ru.  
Proc. Acad. Nat. Sci. Phila. 6 (1852), 209; Amer. J. Sci. [2], 15 (1853), 446; Ann. des Mines [5], 3 (1853), 683; Chem. Gaz. 11 (1853), 145; J. prakt. Chem. 59 (1853), 156; Chem. Centrbl. 1853, 366; Jsb. Chem. 1853, 389, 775.
- 1852: 4. C. PALMSTEDT. Platina funnen vid så kallad skedning af silfvermynt vid Kongl. Myntet i München. Pt.  
Ofvers. Vet. Akad. Förh. Stockholm, 9 (1852), 220.
- 1852: 5. ———. Bericht über die Gold- und Platina-Ausbeute in Russland, im Jahre 1851. Pt.  
Russ. Berg. Journ. 1852, i, 149, 311, 457, 461, 463; Berg u. Hütten Ztg. 12 (1853), 661.
- 1852: 6. C. KARMRODT and E. UHRLAUB. Ueber ein neues Iridiumsalz. (Double chlorids of iridium and sodium and silver.) Ir.  
Ann. Chem. 81 (1852), 120; J. prakt. Chem. 56 (1852), 190; Chem. Centrbl. 1852, 262; Jsb. Chem. 1851, 372.
- 1852: 7. SKOBLIKOFF. Recherches sur quelques combinaisons nouvelles d'iridium. (Irid-ammonium compounds.) Ir.  
Bul. Acad. Sci. St. Pétersb. 11 (1853), 25; Ann. Chem. (Liebig), 84 (1852), 275; Chem. Gaz. 11 (1853), 29; J. prakt. Chem. 58 (1853), 31; Amer. J. Sci. [2], 16 (1853), 412; Chem. Centrbl. 1852, 833; Jsb. Chem. 1852, 428; Mélanges phys. chim. Acad. St. Pétersb. 1 (1852), 400.
- 1852: 8. G. B. BUCKTON. Observations upon a new series of double chlorids containing diplatosammonium. Pt.  
Q. J. Chem. Soc. 5 (1852), 213; Ann. Chem. (Liebig), 84 (1852), 270; J. prakt. Chem. 57 (1852), 367; Chem. Centrbl. 1853, 218; Jsb. Chem. 1852, 425.
- 1852: 9. T. ANDREWS. On the atomic weights of platinum and barium. (Pt = 197.88.) Pt.  
Rept. Brit. Assoc. 1852, ii, 33; Chem. Gaz. 10 (1852), 379; Ann. Chem. (Liebig), 85 (1853), 255; l'Institut, 20 (1852), 346; J. prakt. Chem. 57 (1852), 377; Jsb. Chem. 1852, 425.
- 1852: 10. W. HÄIDINGER. Ueber den Zusammenhang der Körperfarben . . . und der Oberflächenfarben gewisser Körper. (Platinum cyanids and oxalate, palladium chlorid and iridium potassium chlorid.) Pt, Pd, Ir.  
Sitzber. Akad. Wien. 8 (1852), 97; Ann. chim. phys. [3], 42 (1854), 249.

- 1852: 11. W. KNOP. Notiz über den Platinmohr und die Aethylquecksilberverbindung von Sobrero und Selmi. (Platin ethyl compound.) Pt.  
J. prakt. Chem. 56 (1852), 312; Chem. Gaz. 10 (1852), 313; Chem. Centrbl. 1852, 431; Jsb. Chem. 1852, 603.
- 1852: 12. H. ST. CLAIRE DEVILLE. Note sur la température produite par la combustion du charbon dans l'air. (Furnace for fusing platinum.) Pt.  
C. R. 35 (1852), 796; Polyt. J. (Dingler), 127 (1853), 114; Berg u. Hütten Ztg. 12 (1853), 537.
- 1852: 13. A. T. KUPFFER. (Elasticity of platinum.) Pt.  
Ann. obs-phys. centr. Russie (Kupffer). 1852, ii; Bul. Acad. Sci. St. Pétersb. 12 (1854), 129; Mélanges phys. chim. Acad. St. Pétersb. 1 (1853), 632; Jsb. Chem. 1853, 117.
- 1853: 1. H. MÜLLER. Ueber die Palladamine. Inaug. Diss. Göttingen, 1853. Pd.  
Ann. Chem. (Liebig), 86 (1853), 341; Ann. chim. phys. [3], 40 (1854), 321; Amer. J. Sci. [2], 16 (1853), 410; Arch. sci. phys. nat. 23 (1853), 291; J. prakt. Chem. 59 (1853), 29; Chem. Gaz. 11 (1853), 241, 263; Chem. Centrbl. 1853, 241, 261; Jsb. Chem. 1853, 382.
- 1853: 2. A. BÉCHAMP. Faites pour servir à l'histoire analytique du palladium et de l'argent. (Cyanid of palladium and silver.) Pd.  
J. de pharm. [3], 23 (1853), 413; J. prakt. Chem. 60 (1853), 64.
- 1853: 3. R. KERSTING. Ueber Iodbestimmung. (By titration with palladous chlorid.) Pd.  
Ann. Chem. (Liebig), 87 (1853), 19; Ann. chim. phys. [3], 41 (1854), 493; Chem. Gaz. 12 (1854), 156; Chem. Centrbl. 1854, 65; Jsb. Chem. 1853, 647.
- 1853: 4. J. NICKLÉS. Recherches sur le polymorphisme. (Crystallization of palladium and iridium.) Pd. Ir.  
Ann. chim. phys. [3], 39 (1853), 404 (Abstr. Thésis, Fac. des Sc. Paris, July 25, 1853); J. de Pharm. [3], 24 (1853), 5.
- 1853: 5. E. R. SCHNEIDER. Bemerkungen über einige Aequivalentzahlen (des Rhodiums und des Osmiums). Rh, Os.  
Ann. der Phys. (Pogg.), 88 (1853), 314.
- 1853: 6. P. A. BOLLEY. Die bekannte technisch gebrauchten Metalllegirungen in geordneter Zusammenstellung nach Qualität und Quantität der Bestandtheile. (Platinum alloys.) Pt.  
Polyt. J. (Dingler), 129 (1853), 438 (from Bolley's "Handbuch"); Chem. Centrbl. 1854, 786.

- 1853: 7. R. BÖTTGER. Ueber das Verplatiniren gläserner und porzellanener Gefäße. Pt.  
Ber. Deutsch. Nat. Versamml. 1847, 364; Jahrsber. phys. Ver. Frankfurt a M. 1853-54; 1855-56, 24; Polyt. J. (Dingler), 136 (1855), 464; Jsb. Chem. 1855, 851; 1857, 273.
- 1853: 8. P. JEWREINOFF [= JEWREINOW]. (Platiniren von Eisen und Kupfer.) Pt.  
La technologiste; Polyt. Centrbl. 19 (1853), 509; Chem. Centrbl. 1853, 624; Jahrb. Phys. Ver. Frankfurt, 1853-54; Polyt. J. (Dingler), 136 (1855), 464; Polyt. Notizbl. (1853), 168; Chem. tech. Mitth. (Elsner), 4 (1852-54), 154; 12 (1862-63), 139.
- 1853: 9. G. G. STOKES. On the change of refrangibility of light. (Fluorescence of platinocyanids.) Pt.  
Phil. Trans. London, 143 (1853), 395; Proc. Roy. Soc. London, 1850-54, 333; Ann. der Phys. (Pogg.), 96 (1855), 541; Phil. Mag. [4], 10 (1855), 69, 95; Jsb. Chem. 1855, 132.
- 1853: 10. G. G. STOKES. On the metallic reflection exhibited by certain non-metallic substances. (Magnesium platinocyanid.) Pt.  
Phil. Mag. [4], 6 (1853), 398; Ann. der Phys. (Pogg.), 91 (1854), 307; Ann. chim. phys. [3], 46 (1856), 504.
- 1853: 11. G. MAGNUS. Ueber die Verdichtung der Gase an der Oberfläche glatter Körper. (Condensation on platinum sponge.) Pt.  
Ber. Acad. Berlin, 1853, 378; Ann. der Phys. (Pogg.), 89 (1853), 604; Ann. chim. phys. [3], 39 (1853), 344; Phil. Mag. [4], 6 (1853), 334.
- 1853: 12. G. WIEDEMANN and R. FRANZ. Ueber die Wärmeleitungsfähigkeit der Metalle. (Platinum and palladium, p. 513.) Pt, Pd.  
Ann. der Phys. (Pogg.), 89 (1853), 497; Ann. chim. phys. [3], 41 (1854), 107; Arch. sci. phys. nat. 25 (1854), 338.
- 1854: 1. W. P. BLAKE. On the gold and platinum of Cape Blanco. (Oregon.) Pt.  
Amer. J. Sci. [2], 18 (1854), 156; 20 (1855), 79; Jsb. Chem. 1854, 806.
- 1854: 2. H. DUBOIS. De la présence de l'iridium dans l'or de California. Ir.  
Ann. des Mines [5], 6 (1854), 518; Amer. J. Sci. [2], 21 (1856), 205; Jsb. Chem. 1855, 847; Polyt. J. (Dingler), 141 (1856), 109; Bul. Soc. d'Encouragement, Jan. (1856), 31; Polyt. Centrbl. (1855), 1183; Chem. tech. Mitth. (Elsner), 5 (1854-56), 118.
- 1854: 3. ———. Jahresbericht über die Fortschritte des Mineralogie im Jahre 1853. Pt.  
Berg u. Hütten Ztg. 13 (1854), 334.



- 1854: 4. ————. Platin-Fund (in Siebengebirgen). Pt.  
Berg u. Hütten Ztg. 13 (1854), 232, from Casseler Ztg.
- 1854: 5. E. FRÉMY. Nouvelles recherches sur les métaux qui accompagnent le platine dans sa mine. (Decomposition of iridosmium by oxidation in current of air.) Pt, Pd, Ir, Os, Rh, Ru.  
C. R. 38 (1854), 1008; J. prakt. Chem. 62 (1854), 340; J. de Pharm. [3], 26 (1854), 99; l'Institut, 22 (1854), 201; Chem. Centrbl. 1854, 520; Chem. Gaz. 12 (1854), 241; Polyt. J. (Dingler), 133 (1854), 270; Ztsch. anal. Chem. 5 (1866), 120; Jsb. Chem. 1854, 367; J. Chem. Soc. 7 (1854), 256; J. Frank. Inst. [3], 30 (1855), 412; Atheneum, Sept. (1855).
- 1854: 6. C. CLAUS. Beiträge zur Chemie der Platinmetalle. Dorpat, 1854. (Full description of the chemistry of the platinum metals.) Jsb. Chem. 1855, 423, 444, 814, 905. Pt, Pd, Ir, Os, Rh, Ru.
- 1854: 7. C. CLAUS. Ueber die Platinbasen. Pt, Pd, Rh, Ir.  
Bul. Acad. Sci. St. Pétersb. 13 (1855), 97; J. prakt. Chem. 63 (1854), 99; Chem. Centrbl. 1854, 789; Chem. Gaz. 12 (1854), 441; Jsb. Chem. 1854, 369; Mélanges phys. chim. Acad. St. Pétersb. 2 (1854), 130.
- 1854: 8. E. URICOECHEA. Iridium und seine Verbindungen. Inaug. Diss. Göttingen, 1854. (Phosphate, bromid, sulfate, chlorid.) Ir.  
Amer. J. Sci. [2], 18 (1854), 447.
- 1854: 9. G. B. BUCKTON. On the platino-tersulphocyanides and the platino-bisulphocyanides, two new series of salts, and their decompositions. Pt.  
Q. J. Chem. Soc. 7 (1854), 22; J. prakt. Chem. 64 (1855), 65; Ann. Chem. (Liebig), 92 (1854), 280; Chem. Centrbl. 1854, 545; Jsb. Chem. 1854, 379.
- 1854: 10. C. G. WILLIAMS. On the presence of pyridine among the volatile bases in the naphtha from the bitumenous shale from Dorsetshire, and on the fractional crystallization of platinum salts. Phil. Mag. [4], 8 (1854), 209; J. prakt. Chem. 64 (1855), 54. Pt.
- 1854: 11. J. H. GLADSTONE. Notes on some substances which exhibit the phenomena of fluorescence. (Platinum chlorid with potassium iodid.) Pt.  
Edinb. N. Phil. J. 1 (1855), 83; Chem. Gaz. 12 (1854), 420; J. prakt. Chem. 64 (1855), 438; Jsb. Chem. 1855, 133.
- 1854: 12. ————. Benutzung des Irid-osmiums zur Lösung des Zinnes. Os, Ir.  
Arch. der Pharm. 80 (1854), 324; Chem. Centrbl. 1855, 56; Polyt. Notizbl. 9 (1854), 192; Polyt. Centrbl. 25 (1854), 1084.

- 1854: 13. H. HOW. Note on platinum accompanying silver in solution in nitric acid. Pt.  
Q. J. Chem. Soc. 7 (1854), 48; Chem. Gaz. 12 (1854), 209; J. prakt. Chem. 63 (1854), 125; Chem. Centrbl. 1854, 592; Jsb. Chem. 1854, 366.
- 1854: 14. W. LASCH. Auflösung des Platins in Glasretorten (unzweckmässig). Pt.  
J. prakt. Chem. 63 (1854), 344.
- 1854: 15. J. SCHABUS. Crystallogische Untersuchungen. (Mono-, bi-, and tetra-ethylammonium platinum chlorid, p. 43.) Wien, 1855. Sitzber. Acad. Wien, 15 (1855), 200; Jsb. Chem. 1854, 379. Pt.
- 1854: 16. SAVARD. (Plating of copper with platinum.) Pt.  
Pract. Mech. J. 6 (1854), 256; Polyt. J. (Dingler), 131 (1854), 413.
- 1854: 17. A. T. KUPFFER. (Elasticity of torsion of platinum.) Pt.  
C. R. l'obs. cent. Russie, 1854, 1; Jsb. Chem. 1855, 69.
- 1854: 18. T. GRAHAM. On osmotic force. Bakerian Lecture. (Cf. platinochlorid, Q. J. Chem. Soc., 8 : 59, 94.) Pt.  
Phil. Trans. London, 144 (1854), 177; Q. J. Chem. Soc. 8 (1855), 43; Ann. chim. phys. [3], 45 (1855), 5; Arch. sci. phys. nat. 27 (1854), 37.
- 1855: 1. M. BOCKING. Platinerz aus Borneo. (Analysis.) Pt, Pd, Ir, Os, Rh, Ru.  
Ann. Chem. (Liebig), 96 (1855), 243; J. prakt. Chem. 67 (1856), 207.
- 1855: 2. J. W. MALLET. On the crystallization of platinum from fusion. Pt.  
Amer. J. Sci. [2], 20 (1855), 340; J. prakt. Chem. 67 (1856), 252; Chem. Centrbl. 1856, 47; Jsb. Chem. 1855, 420; Chem. Gaz. No. 317; J. Frank. Inst. [3], 31 (1856), 139.
- 1855: 3. E. FRÉMY. Nouvelles recherches sur la mine de platine. (Composition, p. 386; preparation of osmium, 387; ruthenium, 392; iridium, 394; rhodium, 395; salts of rhodium, 398.) Pt, Pd, Os, Ru, Ir, Rh.  
Ann. chim. phys. [3], 44 (1855), 385; Rept. Brit. Assoc. 1855, ii, 63; Jsb. Chem. 1855, 422.
- 1855: 4. L. P. DE SAINT-GILLES. Action de la chaleur sur l'hydrate et sur l'acétate ferriques. (Separation of iridium from platinum by sodium acetate.) Pt, Ir.  
C. R. 40 (1855), 1243; J. prakt. Chem. 16 (1855), 144.

- 1855: 5. D'HENNIN. Procédé pour l'affinage de l'or allié à l'iridium dans les cendres iridifères. Ir.  
C. R. 40 (1855), 1203; Bul. soc. d'encour. (1856), Jan.; Polyt. J. (Dingler), 141 (1856), 109; Chem. tech. Mitth. (Elsner), 5 (1854-56), 102.
- 1855: 6. G. CLEMENTI. Sulli joduri di platino. Pt.  
N. Cimento. 2 (1855), 192; Jsb. Chem. 1855, 420.
- 1855: 7. R. LÖWIG. Doppelverbindungen von Chlorstibäthylum mit Platinchlorid. Pt.  
J. prakt. Chem. 64 (1855), 424 (from Inaug. Diss. Breslau).
- 1855: 8. T. ANDERSON. Preliminary notice on the decomposition of the platinum salts of the organic alkalies. (Pyridin, picolin, and other bases produced by destructive distillation of animal substances.) Pt.  
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- 1855: 9. C. A. WURTZ. (Criticism of Anderson (1855: 8) on platinum bases.) Pt.  
Ann. chim. phys. [3], 45 (1855), 369; Jsb. Chem. 1855, 555.
- 1855: 10. M. PEYRONE. Dell' azione dell' acido nitrico sopra il sal verde di Magnus. Pt.  
Cimento 6 (1855), 872; N. Cimento 2 (1855), 387; Jsb. Chem. 1855, 421.
- 1855: 11. M. PEYRONE. Dell' azione dell' acido nitrico sopra l'isomero giallo del sal di Magnus. Pt.  
Cimento 6 (1855), 874; Jsb. Chem. 1855, 421.
- 1855: 12. A. SCHAFARIK. Ueber die Cyanverbindungen des Platins. Pt.  
Sitzber. Acad. Wien. 17 (1855), 57; J. prakt. Chem. 66 (1855), 385; Chem. Gaz. 13 (1855), 441; Chem. Centrbl. 1855, 721; Jsb. Chem. 1855, 439.
- 1855: 13. R. BÖTTGER. Ueber die Fluorescenz des Kaliumplatin-cyanürs. (Fluorescence in solution.) Pt.  
Ann. der Phys. (Pogg.), 95 (1855), 176; 97 (1856), 333; Phil. Mag. [4], 10 (1855), 69; Jsb. Chem. 1855, 132.
- 1855: 14. G. G. STOKES. On the alleged fluorescence of a solution of platino-cyanide of potassium. Pt.  
Phil. Mag. [4], 10 (1855), 95.

- 1855: 15. H. VOHL. Anwendung des unterschwefligsauren Natrons in der analytischen Chemie. (Action on platinum salts.) Pt.  
J. prakt. Chem. 67 (1856), 177; Ann. Chem. (Liebig), 96 (1855), 241; J. de Pharm. 29 (1856), 74.
- 1855: 16. C. WELTZIEN. Ueber die Krystallformen der Platinsalze der zusammengesetzten Ammoniummoleciüle des Aethyls. Pt.  
Ann. Chem. (Liebig), 93 (1855), 272.
- 1855: 17. C. DE MARNAG. Recherches sur les formes cristallines de quelques composés chimiques. Genève, 1855. (Sodium platino-chlorid, p. 27.) Pt.  
C. R. 42 (1856), 288; Mém. Soc. Phys. Genève, 14 (1858), 202; Jsb. Chem. 1855, 421.
- 1855: 18. ROSELEUR and LANAU. (Plating with platinum.) Pt.  
Polyt. Centrbl. 1855, 57; Polyt. J. (Dingler), 138 (1855), 318; Jsb. Chem. 1855, 852; Polyt. Notizbl. (1855), 56; Chem. tech. Mitth. (Elsner), 5 (1854-56), 172.
- 1855: 19. R. BÖTTGER. (Electroplating copper and brass with platinum; after Jewreynoff.) Pt.  
Polyt. Notizbl. 1855, No. 4; Polyt. Centrbl. 1855, 1210; Polyt. J. (Dingler), 138 (1855), 318; Chem. Centrbl. 1855, 736; Jsb. Chem. 1855, 852.
- 1855: 20. W. HAIDINGER. Herapathit Zangen. (Optical properties of barium and magnesium platino-cyanids.) Pt.  
Sitzber. Acad. Wien, 15 (1855), 82; Jsb. Chem. 1855, 151.
- 1855: 21. A. VOGEL, JR., and C. REISCHAUER. Ueber eine neue Form der bei Löthrohrversuchen angewandten Platinpincetten und Platindrähte. Pt.  
Gelehrtes Anz. München, 41 (1855), Bull. No. 15; Polyt. J. (Dingler), 138 (1855), 44.
- 1855: 22. J. STENHOUSE. On platinized charcoal. Pt.  
Q. J. Chem. Soc. 8 (1855), 105; Ann. chim. phys. [3], 45 (1855), 496; Ann. Chem. (Liebig), 96 (1855), 36; J. de Pharm. 28 (1855), 317; J. prakt. Chem. 66 (1855), 380.
- 1855: 23. A. BAUDRIMONT. Note sur l'inflammabilité de l'hydrogène (par le platine). Pt.  
C. R. 41 (1855), 177; Ann. der Phys. (Pogg.), 96 (1855), 351; J. prakt. Chem. 67 (1856), 187.
- 1855: 24. R. ADIE. On thermo-electric joints formed with the metals antimony, bismuth, and palladium. Pd.  
Q. J. Chem. Soc. 8 (1855), 36.

- 1856: 1. J. B. BOUSSINGAULT. Sur un gisement de platine signalé dans un filon de la province d'Antioquia. Observations inédites sur les alluvions aurifères et platinifères du Choco. Pt.  
C. R. 42 (1856), 917; l'Institut, 24 (1856), 191; Jsb. Chem. 1856, 829.
- 1856: 2. C. SCHEIBLER. Beiträge zur Kenntniss der Lithionsalze. (Lithium platinchlorid.) Pt.  
J. prakt. Chem. 67 (1856), 485.
- 1856: 3. W. F. SALM-HORSTMAR. Ueber Chlorplatinaluminum. Pt.  
Ann. der Phys. (Pogg.), 99 (1856), 638; J. prakt. Chem. 70 (1857), 121; Jsb. Chem. 1856, 413.
- 1856: 4. A. W. HOFMANN and A. CAHOURS. Recherches sur les bases phosphorées. Pt.  
C. R. 43 (1856), 1092; Ann. Chem. (Liebig), 104 (1857), 1; Phil. Trans. 147 (1857), 595; Ann. chim. phys. [3], 51 (1857), 5; J. prakt. Chem. 70 (1857), 364; J. Chem. Soc. 11 (1858), 56.
- 1856: 5. C. CLAUS. Ueber einige Rhodanverbindung. (Platinumthiocyanate, p. 48.) Pt.  
Ann. Chem. (Liebig), 99 (1856), 48; Ann. chim. phys. [3], 49 (1857), 101; J. prakt. Chem. 70 (1857), 52; J. de Pharm. 31 (1857), 125; Chem. Gaz. 14 (1856), 344; Chem. Centrbl. 1856, 730; Jsb. Chem. 1856, 443.
- 1856: 6. C. CLAUS. Ueber die Ammoniummolecüle der Metalle. (Theoretical article on the metal-ammonium bases.) Pt, Pd, Ir, Os, Rh, Ru.  
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- 1856: 7. P. WESELSKY. Ueber einige neue der Formel  $R_2Pt_2Cy_3nHO$  entsprechende Platincyanverbindungen, ferner über rothes  $HPtCy_2$ , 5HO und gelbes  $MgPtCy_2$ , 6HO. Pt.  
Sitzber. Acad. Wien, 20 (1856), 282; J. prakt. Chem. 69 (1856), 276; Chem. Centrbl. 1856, 779; Jsb. Chem. 1856, 440.
- 1856: 8. C. WELTZIEN. Ueber die Ammoniummolecüle der Metalle. (Theoretical consideration of metal-ammonium bases.) Pt, Pd, Ir, Os, Rh, Ru.  
Ann. Chem. (Liebig), 97 (1856), 19; 100 (1856), 108; Chem. Centrbl. 1856, 114; Jsb. Chem. 1856, 313, 414.
- 1856: 9. C. GRIMM. Beitrag zur Kenntniss der Platinbasen. Pt.  
Ann. Chem. (Liebig), 99 (1856), 67; J. prakt. Chem. 69 (1856), 420; Phil. Mag. [4], 12 (1856), 301; Chem. Centrbl. 1856, 750; Jsb. Chem. 1856, 415.

- 1856: 10. C. GRIMM. Ein neues Platinsalz. (Double platosamin ammonium chlorid.) Pt.  
Ann. Chem. (Liebig), 99 (1856), 95; J. prakt. Chem. 70 (1857), 61; Jsb. Chem. 1856, 415.
- 1856: 11. W. GIBBS and F. A. GENTH. Researches on the ammonia-cobalt bases. (Platinum chlorids of cobalt-ammonium bases.) Pt.  
Smith. Cont. Knowl. 9 (1856); Amer. J. Sci. [2], 23 (1857), 234, 319; 24 (1857), 86; J. prakt. Chem. 72 (1857), 148; Ann. Chem. (Liebig), 104 (1857), 150, 295; Chem. Gaz. 15 (1857), 141, 165, 188, 250, 266, 383, 404; Chem. Centrbl. 1858, 129, 257; Jsb. Chem. 1857, 234.
- 1856: 12. H. SAINTE-CLAIRE DEVILLE. Action de l'acide iodhydrique sur l'argent. (Palladium acted on by hydriodic acid, but platinum almost unacted on.) Pt, Pd.  
C. R. 42 (1856), 894; Ann. Chem. (Liebig), 101 (1857), 196; J. prakt. Chem. 69 (1856), 420.
- 1856: 13. W. KEFERSTEIN. Ueber die Krystallformen einiger chemischen Verbindungen. (Ammonium iridium chlorid, ammonium rhodium chlorid, barium palladium cyanid, and potassium platinum thiocyanate.) Pt, Pd, Ir, Rh.  
Ann. der Phys. (Pogg.), 99 (1856), 275; J. prakt. Chem. 69 (1856), 303; Jsb. Chem. 1856, 420, 442, 445.
- 1856: 14. CARANZA. Note sur un nouveau procédé de fixation pour les épreuves photographiques, au moyen du chlorure acide de platine. (Only title.) Pt.  
C. R. 42 (1856), 344; Chem. Centrbl. 1856, 192.
- 1856: 15. H. SAINTE-CLAIRE DEVILLE. Mémoire sur la production des températures très élevées. (Fusion of platinum, p. 198.) Pt.  
Ann. chim. phys. [3], 46 (1856), 182; Ann. Chem. (Liebig), 102 (1857), 326; Bul. Soc. Encour. Paris, 55 (1856), 286; Polyt. J. (Dingler), 140 (1856), 428; Jsb. Chem. 1856, 315.
- 1856: 16. H. H. LANDOIS. (Plating metals with platinum in the cold.) Pt.  
Cosmos, rev. encyclop. Sept. (1856), 309; Polyt. J. (Dingler), 142 (1856), 157; J. Frank. Inst. [3], 32 (1856), 265; Soc. Encour. Nat. Indust. Paris (1855), Dec. 25.
- 1856: 17. A. SMEE. (Method of depositing platinum black on platinum and silver.) Pt.  
Polyt. Notizbl. 1856, No. 21; Polyt. J. (Dingler), 142 (1856), 157; Chem. Centrbl. 1857, 96.

- 1856: 18. V. REGNAULT. Mémoire sur la chaleur spécifique de quelques corps simples. (Specific heat of osmium, p. 262; rhodium and iridium, 263.) Os, Rh, Ir.  
Ann. chim. phys. [3], 46 (1856), 257; Ann. der Phys. (Pogg.), 98 (1856), 401; Phil. Mag. [4], 12 (1856), 493; Arch. sci. phys. nat. 31 (1856), 316; N. Cimento, 3 (1856), 442; Jsb. Chem. 1856, 41.
- 1857: 1. A. A. DAMOUR and A. DESCLOIZEAUX. Examen de divers échantillons de sables aurifères et platinifères. Pt.  
Ann. chim. phys. [3], 51 (1857), 445.
- 1857: 2. ————. Price of platinum (in 1857). Pt.  
Ann. der Phys. (Pogg.), 101 (1857), 644; Polyt. J. (Dingler), 146 (1857), 77.
- 1857: 3. H. SAINTE-CLAIRE DEVILLE and H. DEBRAY. Des métaux du platine et de leur traitement par la voie sèche. Pt, Pd, Ir, Os, Rh, Ru.  
C. R. 44 (1857), 1101; Ann. Chem. (Liebig), 104 (1857), 227; J. prakt. Chem. 71 (1857), 371; l'Institut, 25 (1857), 173, 181; Chem. Gaz. 15 (1857), 310; Cimento, 6 (1857); Chem. Centrbl. 1857, 433; Polyt. J. (Dingler), 145 (1857), 44; Jsb. Chem. 1857, 259.
- 1857: 4. A. MUCKLÉ and F. WÖHLER. Ueber den Platingehalt der Platinrückstände. (Separation of platinum and iridium.) Pt, Ir.  
Ann. Chem. (Liebig), 104 (1857), 368; J. prakt. Chem. 73 (1858), 318; Polyt. J. (Dingler), 149 (1858), 237; Chem. Centrbl. 1858, 254; Jsb. Chem. 1857, 262.
- 1857: 5. O. KÖTTIG. Krystallisirtes Platin. Pt.  
J. prakt. Chem. 71 (1857), 190; Jsb. Chem. 1857, 261.
- 1857: 6. E. WYSOCKY. Ueber die Affinirung des osmium-iridium-haltigen Goldes vom Stabs Capitain Belozerow. Os, Ir.  
Oester. Ztsch. für Berg- und Hüttenwesen, 1857, No. 26; Chem. Centrbl. 1857, 665.
- 1857: 7. T. OPPLER. Ueber die Iodverbindungen des Iridiums. Inaug. Diss. Göttingen, 1857. Ir.  
Jsb. Chem. 1857, 263.
- 1857: 8. V. SCHWARZENBACH. (Potassium platinocyanid and morphin, etc.) Pt.  
Vierteljahrssch. prakt. Pharm. 6 (1857), 422; Jsb. Chem. 1857, 602.
- 1857: 9. A. W. HOFMANN. Contributions towards the history of the phosphorus-, arsenic-, and antimony-bases. (Platinum salts.) Pt.  
Proc. Roy. Soc. London, 8 (1856-57), 500; Ann. Chem. (Liebig), 103 (1857), 357; J. de Pharm. 34 (1858), 137; Chem. Centrbl. 1857, 947.

- 1857: 10. R. BÖTTGER. Palladiumchlorür, ein ausgezeichnetes Reagens für verschiedene Gase. Pd.  
 Jsber. phys. Ver. Frankfurt a. M. 1857-58, 45; Ann. der Phys. (Pogg.), 106 (1859), 495; J. prakt. Chem. 76 (1859), 233; N. Jhrbuch. prakt. Pharm. 11 (1859), 263; Polyt. J. (Dingler), 152 (1859), 76; Rép. chim. pur. 1 (1859), 402; Chem. Centrbl. 1859, 321; Jsb. Chem. 1859, 257; Polyt. Notizbl. 14 (1859), 102; Polyt. Centrbl. 25 (1859), 683; Chem. tech. Mitth. (Elsner), 8 (1858-59), 55.
- 1857: 11. Q. SELLA. Sulla forme cristalline di alcuni sali di platino e del boro adamantino. (Crystal forms of platinum bases.) Pt.  
 Mem. Accad. Torino [2], 17 (1858), 337; Cimento, 5 (1857), 81; 7 (1858), 228; Arch. sci. phys. nat. 34 (1857), 330; Jsb. Chem. 1857, 261; Ann. der Phys. (Pogg.), 100 (1857), 646.
- 1857: 12. H. DE SENARMONT. Rammelsberg: Die neueste Forschungen in der krystallinischen Chemie, Leipzig, 1857-8. (Birefractive crystals.) Ru.  
 Jsb. Chem. 1857, 265.
- 1857: 13. W. J. GRAILICH and V. VON LANG. Untersuchungen über die physikalischen Verhältnisse krystallisirter Körper. (Double platinoeyanids, p. 16.) Pt.  
 Sitzber. Acad. Wien, 27 (1857), 3; Jsb. Chem. 1858, 235; Kryst. opt. Untersuchungen, Wien und Olmütz, 1858, 99.
- 1857: 14. A. DESCLOIZEAUX. Propriétés optiques biréfringentes des cyanure de barium et de platine; cyanure de magnesium et de platine: chlorure de platine et d'éthylammoniaque. Pt.  
 Ann. des Mines [5], 11 (1857), 301, 306, 324; 14 (1858), 393.
- 1857: 15. H. SAINTE-CLAIRE DEVILLE. Mémoire sur le silicium. (Action of silicon on platinum, p. 66.) Pt.  
 Ann. chim. phys. [3], 49 (1857), 62; J. de Pharm. 31 (1857), 116.
- 1857: 16. H. SAINTE-CLAIRE DEVILLE. Schmelzung schwer schmelzbaren Metalle. Pt.  
 Polyt. Centrbl. 1857, 605; Chem. Centrbl. 1857, 461.
- 1857: 17. R. BÖTTGER. Verhalten . . . des Platins zu dem geschmolzenen chlorsauren Kali. Pt.  
 N. Rep. für Pharm. (Buchner), 6 (1857), 247; Chem. Centrbl. 1857, 636.
- 1857: 18. C. G. MOSANDER. Filtrerings-apparater af Platina. Pt.  
 Oefver. Akad. Förh. Stockholm, 14 (1857), 263.
- 1857: 19. W. C. HERAEUS. Preis Platingeräthe. Pt.  
 Ann. der Phys. (Pogg.), 101 (1857), 644; Chem. Centrbl. 1857, 844.



- 1857: 20. C. F. SCHÖNBEIN. Ueber einige neue Reihen chemischer Berührungswirkungen. (Influence of platinum sponge.) Pt. Abh. bayer. Akad. Wiss. 8 (1857), 37.
- 1857: 21. A. BERTIN. Sur la formation de l'eau par des lames de platine qui ont servi à transmettre un courant électrique. Pt. Ann. chim. phys. [3], 51 (1847), 450; C. R. 44 (1857), 1273; J. prakt. Chem. 71 (1857), 371; Chem. Centrbl. 1857, 607.
- 1857: 22. J. MÜLLER. Abnahme der Elektrizitätsleitung in Metallen bei starke Temperatur-Erhöhung. (Leitungswiderstand des Platins.) Pt. Programm d. Gymnasiums zu Wesel, 1857; Ann. der Phys. (Pogg.), 103 (1858), 176; Jsb. Chem. 1858, 110.
- 1857: 23. L. CAILLETET. De l'influence de l'hydrogène naissant sur l'amalgamation. Pt. C. R. 44 (1857), 1250; Jsb. Chem. 1857, 249.
- 1858: 1. S. BLEEKRODE. Platinerz von Borneo. Pt. Ann. der Phys. (Pogg.), 103 (1858), 656; J. de Pharm. 34 (1858), 219; J. prakt. Chem. 74 (1858), 361; Polyt. J. (Dingler), 151 (1859), 156; Pharm. J. and Trans. 18 (1859), 32; Jsb. Chem. 1858, 675.
- 1858: 2. W. HENKE. Verbindungen der Nitrile mit Chlorüren. (Cyanethyl und Platinchlorid.) Pt. Ann. Chem. (Liebig), 106 (1858), 280; J. prakt. Chem. 75 (1858), 204; J. de Pharm. 34 (1858), 448.
- 1858: 3. K. VON THANN. Ueber das Platincyanäthyl. Pt. Sitzber. Acad. Wien, 31 (1858), 26; Ann. Chem. (Liebig), 107 (1858), 315; J. prakt. Chem. 75 (1858), 190; J. de Pharm. 34 (1858), 449; Rép. chim. pur. 1 (1859), 137; Chem. Gaz. 17 (1859), 41; Chem. Centrbl. 1858, 787; Jsb. Chem. 1858, 235.
- 1858: 4. C. G. WILLIAMS. (Platinchlorid and quinolin.) Pt. Chem. Gaz. 16 (1858), 346; J. prakt. Chem. 76 (1859), 251; Jsb. Chem. 1858, 357.
- 1858: 5. W. GIBBS and F. A. GENTIL. Preliminary notice of a new base containing osmium and the elements of ammonia. Os, Ir. Amer. J. Chem. [2], 25 (1858), 248; Chem. Centrbl. 1859; 130; Rép. chim. pur. 1 (1859), 326; Proc. Amer. Assoc. 1858, 197; Jsb. Chem. 1858, 214.
- 1858: 6. A. SOUCHAY and E. LENNSEN. Ueber die Oxalate der schweren Metalloxyde. (Oxalsaaures Platinoxydul Natron.) Pt. Ann. Chem. (Liebig), 105 (1858), 256; J. prakt. Chem. 74 (1858), 170.

- 1858: 7. C. CLAUS. Ueber die Reduction des Iridiumchlorids ( $\text{IrCl}_2$ ) in niedere Chlorstufen. Ir.  
Ann. Chem. (Liebig), 107 (1858), 129; Ann. chim. phys. [3], 54 (1858), 423; J. prakt. Chem. 76 (1859), 24; Rép. chim. pur. 1 (1859), 86; Jsb. Chem. 1858, 210.
- 1858: 8. C. W. HEMPEL. Eisenoxydsalz mit caustischem Alkali als Reductionsmittel. (Reduction of platinum chlorid by ferrous sulfate and formation of platinum black.) Pt.  
Ann. Chem. (Liebig), 107 (1858), 97; J. prakt. Chem. 75 (1858), 444; Polyt. J. (Dingler), 149 (1858), 444; Chem. News, 1 (1860), 107; Jsb. Chem. 1858, 190.
- 1858: 9. J. SPILLER. On some remarkable circumstances tending to disguise the presence of various acids and bases in chemical analysis. (Action of citric acid on platinum dioxid.) Pt.  
Q. J. Chem. Soc. 10 (1858), 110; J. de Pharm. 33 (1858), 54.
- 1858: 10. A. F. NOGUÈS. Influences des hautes températures sur l'état moléculaire de certains corps. (Platinum crystals.) Pt.  
C. R. 47 (1858), 832; Chem. Centrbl. 1859, 16; Jsb. Chem. 1858, 209.
- 1858: 11. F. CRACE-CALVERT and R. JOHNSON. On the expansion of metals, alloys and salts (specific gravity and expansion of platinum.) Pt.  
Rep. Brit. Assoc. 28 (1858), 46; Jsb. Chem. 1859, 10.
- 1858: 12. L. ELSNER. Ueber die Flüchtigkeit einiger Körper in der Weissglühhitze. (Sublimation of platinum, palladium and iridium.) Pt, Pd, Ir.  
Chem. tech. Mitth. (Elsner), 7 (1857-58), 36; J. prakt. Chem. 99 (1866), 257; Jsb. Chem. 1866, 35.
- 1858: 13. W. E. NEWTON. (Platinum alloys.) Pt, Pd, Ir, Rh.  
Repertory Pat. Invent. 1858, 375; Pharm. J. and Trans. 18 (1859), 233; Polyt. J. (Dingler), 148 (1858), 415; Jsb. Chem. 1858, 208.
- 1858: 14. C. BRUNNER. Bereitung von Platinschwarz. Pt.  
Mitth. Naturf. Gesel. Bern, 1858, 83; Ann. Chem. (Liebig), 109 (1859), 253; Ann. der Phys. (Pogg.), 105 (1858), 496; Rép. chim. pur. 1 (1859), 294; Rép. chim. appl. 1 (1859), 211; Chem. Centrbl. 1859, 30; Jsb. Chem. 1858, 209; Chem. News, 1 (1860), 179; Le Monde Sci. Mar. 1 (1860).
- 1858: 15. T. L. PHIPSON. La force catalytique ou études sur les phénomènes de contact. (Combustion under the influence of platinum, etc.) (Mémoire couronné par la Soc. Holland. des Sci., Haarlem, 1858.) Pt, Pd, Rh.  
Nat. Verh. d. Maatsch. Wet. Haarlem, 14 (1861), 1.

- 1858: 16. C. F. SCHÖNBEIN. Ueber den Einfluss des Platins auf chemisch-gebundenen Sauerstoff. Pt.  
Verh. Naturf. Gesel. Basel, 2 (1858), 35; Gelehr. Anz. München, 47 (1858), 89; Ann. chim. phys. [3], 55 (1859), 216; Ann. der Phys. (Pogg.), 105 (1858), 258; J. prakt. Chem. 75 (1858), 101; Jsb. Chem. 1858, 56.
- 1858: 17. W. J. GRAILICH. Ueber Fluorescenz. (Magnesium platino-cyanid.) Pt.  
Verh. Akad. Presburg, 2 (1857), 11; Jsb. Chem. 1858, 3.
- 1858: 18. F. CRACE-CALVERT and R. JOHNSON. Sur la conductibilité de la chaleur par les métaux et leurs alliages. (Conductivity of platinum for heat.) Pt.  
C. R. 47 (1858), 1069; Phil. Trans. London, 148 (1858), 349; Polyt. J. (Dingler), 152 (1859), 125; Jsb. Chem. 1858, 110.
- 1858: 19. A. ARNDTSEN. Ueber den galvanischen Leitungswiderstand der Metalle bei verschiedenen Temperaturen. Pt.  
Ann. der Phys. (Pogg.), 104 (1858), 1; Ann. chim. phys. [3], 54 (1858), 440.
- 1858: 20. A. MATTHIESSEN. Ueber die electrische Leitungsfähigkeit der Metalle. Pt, Pd.  
Ann. der Phys. (Pogg.), 103 (1858), 428; Phil. Trans. London, 148 (1858), 383; Phil. Mag. [4], 16 (1858), 219; Ann. chim. phys. [3], 54 (1858), 255; Arch. sci. ph. nat. [2], 3 (1858), 310; l'Institut, 26 (1858), 402; Chem. Centrbl. 1858, 411; Jsb. Chem. 1858, 108; Cimento, 17 (1863), 47.
- 1859: 1. S. BLEEKRODE. Platinerz von Goenoeng Lawack auf Borneo. Pt.  
Ann. der Phys. (Pogg.), 107 (1859), 189; J. prakt. Chem. 77 (1859), 384; Rép. chim. pur. 1 (1859), 374; Jsb. Chem. 1859, 766.
- 1859: 2. ———. American platinum. (Vein of platinum and gold in Missouri.) Pt.  
Chem. News, 1 (1859), 36.
- 1859: 3. WEIL. (Platinerze aus Californien.) Pt.  
Génie. Indust. 17 (1859), 262; Polyt. J. (Dingler), 153 (1859), 41; Jahrb. der Miner. 1860, 354; Jsb. Chem. 1859, 766; Berg u. Hütten Ztg. 19 (1860), 20; 20 (1861), 270; Berggeist, 5 (1860), No. 57.
- 1859: 4. W. HAIDINGER. Die grosse Platinstufe im K. K. Hof-Mineralien-Cabinet (Wien). Geschenk des Fürsten Anatole von Demidoff. (From Nischnei-Tagilsk.) Pt.  
Sitzber. Acad. Wien, 35 (1859), 345; Jsb. Chem. 1859, 766.

- 1859: 5. SORÈZE. Krystallisation des Platins. Pt.  
Berggeist, 4 (1859), No. 48; Berg u. Hütten Ztg. 19 (1860), 27.
- 1859: 6. M. H. JACOBI (par Pelouze présenté). Médailles frappées avec  
des alliages de platine et iridium. Pt, Ir.  
C. R. 49 (1859), 896; J. prakt. Chem. 80 (1860), 499; Chem. News,  
1 (1860), 23; Polyt. J. (Dingler), 154 (1859), 118; Jsb. Chem.  
1859, 254.
- 1859: 7. M. H. JACOBI (par Pelouze présenté). Un l'ingot d'iridium  
fondu. (267 grams weight.) Ir..  
C. R. 49 (1859), 897; J. prakt. Chem. 80 (1860), 499.
- 1859: 8. C. CLAUS. Neue Beiträge zur Chemie der Platinmetalle.  
Pt, Pd, Ir, Os, Rh, Ru.  
I. Ueber das Ruthenium verglichen mit dem ihm ähnlichen  
Osmium. Bull. 1 : 97.  
II. A. Einiges Allgemeines über die Platinmetalle und einiges  
besonders über das Ruthenium, 2 : 158.  
B. Ueber das Rhodium im Vergleich zum Iridium, 2 : 171.  
III. A. Ueber ammoniumhaltige Rutheniumbasen, 4 : 454.  
B. Ueber die Darstellung des Rutheniumsalzes und über  
die verschiedenen Methode des Aufschliessens des  
Osmium-Iridiums, 4 : 465.  
C. Ein Paar Worte über die Cyanverbindungen, nament-  
lich das Osmiumeyankali, 4 : 482.  
IV. Ueber das Osmium, 6 : 145.  
(Original analysis of Ruthenium "tetrachlorid," 1 : 107.)  
Bull. Acad. Sci. St. Pétersb. 1 (1860), 97; 2 (1860), 158; 4 (1862),  
453; 6 (1863), 145; Ann. chim. phys. [3], 59 (1860), 111; J. prakt.  
Chem. 79 (1860), 28; 80 (1860), 282; 85 (1861), 129; 90 (1863), 65;  
J. de Pharm. 37 (1860), 391; Chem. Centrbl. 1859, 961; 1860, 674,  
689; 1862, 121, 129; 1864, 497; Chem. News, 3 (1861), 194, 257; 4  
(1861), 310; 7 (1863), 115, 121; Rép. chim. pur. 2 (1860), 211; 3  
(1861), 121; 4 (1862), 450; Bul. soc. chim. [2], 3 (1865), 115;  
Amer. J. Sci. [2], 29 (1860), 425; 34 (1862), 183, 213; Ztsch. Chem.  
5 (1862), 117; J. anal. Chem. 1 (1862), 366; 5 (1866), 117; Jsb..  
Chem. 1859, 247; 1860, 204, 742; 1861, 320; 1863, 295; Mélanges  
phys. chim. Acad. St. Pétersb. 4 (1860), 1, 294; 5 (1861), 87; 5  
(1863), 439.
- 1859: 9. H. SAINTE-CLAIRE DEVILLE and H. DEBRAY. Du platine et  
des métaux qui l'accompagnent. (Properties, general, p. 388;  
osmium, 392; ruthenium, 405; palladium, 413; alloys, 414; rho-  
dium, 415; platinum, 419; iridium, 431; alloys, 433; iridosmium,  
437; analysis, 439; assay, 453; cupellation, 457; assay of residues, .

463; assay of iridosmium, 470; metallurgy, 484; extraction of platinum by fusion, 489; preparation of alloys, 493.)

Pt, Pd, Ir, Os, Rh, Ru.

Ann. chim. phys. [3], 56 (1859), 385; Anñ. des Mines [5], 16 (1859), 1; Ann. Chem. (Liebig), 111 (1859), 209; 114 (1860), 78; Ann. der Phys. (Pogg.), 107 (1859), 214; J. de Pharm. [3], 35 (1859), 336; C. R. 48 (1859), 731; l'Institut, 27 (1859), 118; Pharm. J. and Trans. [2], 1 (1859), 414, 470; Polyt. J. (Dingler), 153 (1859), 38; 154 (1859), 130, 199, 287, 383; Chem. News, 1 (1860), 5, 15, 85; Chem. Centrbl. 1859, 559, 668; Rép. chim. pur. 1 (1859), 325, 537; Rép. chim. appl. 1 (1859), 435; Amer. J. Sci. [2], 29 (1860), 113, 373, 379; J. Frank. Inst. [3], 40 (1860), 21; Jsb. Chem. 1859, 230, 767; Berg u. Hütten Ztg. 19 (1860), 20, 256, 260, 272; Chem. tech. Mitth. (Elsner), 9 (1859-60), 125; Polyt. Centrbl. 26 (1860), 960; Polyt. Centrhalles, 10 (1859), 542.

1859: 10. H. DULLO. Ueber Löslichkeit des Platins in Königswasser.

Pt.

J. prakt. Chem. 78 (1859), 369; Chem. News, 1 (1860), 204; Rép. chim. pur. 2 (1860), 114; Rép. chim. appl. 2 (1860), 183; Jsb. Chem. 1859, 256; J. chim. méd. [4], 6 (1860), 259; Berg u. Hütten Ztg. 19 (1860), 352; Chem. tech. Mitth. (Elsner), 10 (1860-61), 126.

1859: 11. W. EICHLER. Beiträge zur Kenntniss einiger Osmiumverbindungen. (Potassium osmite, osmichlorid, and ammonio-silver osmichlorid.)

Os.

Bul. Soc. Nat. Moscou, 32, i, (1859), 152; Archiv Russ. 19 (1860), 278; Jsb. Chem. 1860, 214.

1859: 12. W. KNOP. Notiz über die Bereitung der Platinecyaniddoppelsalze.

Pt.

Chem. Centrbl. 1859, 17; Rép. chim. pur. 1 (1859), 249; Jsb. Chem. 1859, 274.

1859: 13. G. WERTHER. Notiz über Magnesiumplatinecyanür.

Pt.

J. prakt. Chem. 76 (1859), 186; Chem. Gaz. 17 (1859), 448; Chem. Centrbl. 1859, 629; Jsb. Chem. 1859, 274.

1859: 14. V. SCHWARZENBACH. Verbindungen der Alkaloïde mit Platinecyanür.

Pt.

Vierteljahrsh. prakt. Pharm. 8 (1859), 516; Chem. Centrbl. 1860, 304.

1859: 15. W. KNOP. Ueber eine Eigenschaft des Platinsalmiaks, Notiz über ein Zersetzungsproduct des Platinsalmiaks. (Zerstäuben beim Erhitzen; mit Natronlauge gekocht und mit Essigsäure versetzt, gibt Niederschlag.)

Pt.

Chem. Centrbl. 1859, 241, 352; Jsb. Chem. 1859, 256.

- 1859: 16. J. SCHLOSSBERGER. Kleesäure aus Alkohol durch Platinchlorid. Pt.  
Ann. Chem. (Liebig), 110 (1859), 247; Rép. chim. pur. 1 (1859), 419.
- 1859: 17. C. A. MARTIUS. Ueber einige Borverbindungen. (Borplatin, p. 81.) Pt.  
Ann. Chem. (Liebig), 109 (1859), 79; J. prakt. Chem. 77 (1859), 125; Chem. Centrbl. 1859, 221; Jsb. Chem. 1858, 210.
- 1859: 18. E. BECQUEREL. Recherches sur divers effets lumineux qui résultant de l'action de la lumière sur les corps. (Optical properties of the platinocyanids, p. 140.) Pt.  
C. R. 49 (1859), 27; Ann. chim. phys. [3], 57 (1859), 40; Arch. Sci. phys. nat. 6 (1859), 21; Phil. Mag. 18 (1859), 524.
- 1859: 19. C. B. GREISS. Ueber die Fluorescenz des Magnesium Platinocyanür. Pt.  
Ann. der Phys. (Pogg.), 106 (1859), 645; Jsb. Chem. 1859, 275.
- 1859: 20. V. REGNAULT. Une anomalie de la chaleur spécifique d'échantillons d'iridium. (Owing to osmium present.) Ir, Os.  
C. R. 49 (1859), 897; J. prakt. Chem. 80 (1860), 500.
- 1859: 21. G. JENZSCH. Universal Platintriangle. Pt.  
Polyt. J. (Dingler), 151 (1859), 425.
- 1859: 22. H. DULLO. Ueber das Platiniren von Glas und Porcellan (and solution of platinum in aqua regia; cf. 1859 : 10). Pt.  
J. prakt. Chem. 78 (1859), 367; Polyt. J. (Dingler), 157 (1860), 152; J. chim. méd. [4], 6 (1860), 258; J. Frank. Inst. [3], 42 (1861), 414; Bul. Soc. Encour. Nat. Indust. Paris.
- 1859: 23. L. ELSNER. Porzellanflächen mit einem starken Ueberzuge von Platina zu überziehen. Pt.  
Chem. tech. Mitth. (Elsner), 9 (1859-60), 124; Chem. News, 4 (1861), 13.
- 1859: 24. C. F. VASSEROT. Plating glass with platinum and palladium. Pt, Pd.  
Repert. of Pat. Invent. [3], 33 (1859), 485; Polyt. J. (Dingler), 153 (1859), 42; Polyt. Centrhal., 10 (1859), 576; Chem. tech. Mitth. (Elsner), 9 (1859-60), 67.
- 1859: 25. WILD. Einfache Methode, Kupfer und Messing auf sogenanntem nassen Wege mit Platin zu überziehen. Pt.  
Arch. Pharm. 148 (1859), 112; Chem. Centrbl. 1859, 541; Polyt. J. (Dingler), 153 (1859), 238; Polyt. Centrhal., 10 (1859), 560; Chem. tech. Mitth. (Elsner), 9 (1859-60), 126.

- 1859: 26. C. F. SCHÖNBEIN. Ueber die katalytische Zersetzung des Wasserstoffsuperoxydes durch metallisches Platin. Pt. Gelehrte Anz. München, 49 (1859), 169; Verh. Natf. Gesel. Basel, 2 (1860), 280; Ann. der Phys. (Pogg.), 109 (1860), 130; Ann. chim. phys. [3], 58 (1860), 486.
- 1859: 27. C. F. SCHÖNBEIN. Beiträge zur nähern Kenntniss des Sauerstoffes. Pt. Gelehrte Anz. München, 49 (1859), 529; Verh. Natf. Gesel. Basel, 2 (1860), 420; Ann. chim. phys. 59 (1860), 102; J. prakt. Chem. 79 (1860), 65; Ztsch. Chem. anal. Chem. 1 (1862), 9; Ann. der Phys. (Pogg.), 112 (1861), 281.
- 1859: 28. C. F. SCHÖNBEIN. Ueber die chemische Polarisation des Sauerstoffes. Pt. J. prakt. Chem. 78 (1859), 88; Ann. chim. phys. [3], 58 (1860), 479; Verh. Natf. Gesel. Basel, 2 (1860), 251; Ann. der Phys. (Pogg.), 108 (1859), 471; Chem. News, 1 (1860), 109, 254; Phil. Mag. 18 (1859), 510.
- 1859: 29. M. H. JACOBI. Note sur l'emploi d'une contre-batterie de platine aux lignes électro-télégraphiques. Pt. C. R. 49 (1859), 610.
- 1860: 1. V. COTTA. Krystallisirtes gediegenes Platin. Pt. Berg und Hütten Ztg. 19 (1860), 495; Jahrbuch Min. 1861, 327; Jsb. Chem. 1860, 743.
- 1860: 2. M. H. JACOBI. Sur le platine et son emploi comme monnaie, St. Pétersburg, 1860. 8°.
- 1860: 3. ———. Ueber die Gewinnung von Roheisen, Kupfer, Gold und Platin in den Kronsberg und Hüttenwerken des Uralgebirges im Jahre 1858. Pt. Russ. Berg. Journ. 1860; Berg und Hütten Ztg. 19 (1860), 489.
- 1860: 4. H. SAINTE-CLAIRE DEVILLE and H. DEBRAY. De la fusion et du moulage du platine. Pt. C. R. 50 (1860), 1038; J. prakt. Chem. 80 (1860), 500; Chem. News, 2 (1860), 24; Chem. Centrbl. 1860, 639; l'Institut, 28 (1860), 194; Polyt. J. (Dingler), 157 (1860), 64; Amer. J. Sci. [2], 30 (1860), 158; Jsb. Chem. 1860, 205; Rép. chim. appl. 2 (1860), 220; J. Frank. Inst. [3], 40 (1860), 123; Berg u. Hütten Ztg. 20 (1861), 170.
- 1860: 5. H. SAINTE-CLAIRE DEVILLE and H. DEBRAY. De la métallurgie du platine et des métaux qui l'accompagnent. (Assay, Ann. chim. phys. 61 : 8; cupellation, 12, 30; direct fusion, 57; treatment of ores in dry way, 67; extraction of iridium and rhodium, 76;

ruthenium and palladium, 78; treatment of the platinum of old Russian coin, 88.) Pt, Pd, Ir, Os, Rh, Ru.

Ann. des Mines [5], 18 (1860), 71, 325; Ann. chim. phys. [3], 61 (1861), 5; Polyt. J. (Dingler), 165 (1862), 198; Polyt. Centrbl. 27 (1861), 1263; Jsb. Chem. 1861, 881; Berg u. Hütten Ztg. 21 (1862), 76; Chem. tech. Mitth. (Elsner), 12 (1862-63), 138.

1860: 6. W. GIBBS. Researches on the platinum metals. (Ammonium compounds of osmium and palladium; nitric acid compounds of iridium.) Os, Pd, Ir.

Amer. J. Sci. [2], 29 (1860), 427; Jsb. Chem. 1860, 217; Chem. News, 2 (1860), 179.

1860: 7. BOEDEKER. Die Beziehung zwischen Dichte und Zusammensetzung bei festen und liquiden Stoffen. Leipzig, 1860. (Composition and specific gravity of platinum and iridium chlorids and platinum iodids.) Pt, Ir.

Jsb. Chem. 1860, 16.

1860: 8. H. SCHIFF. Die Polysulfurete der Schwermetalle. (Platinum.) Pt.

Ann. Chem. (Liebig), 115 (1860), 73.

1860: 9. C. KLIPPEL. Ueber das Methplumbäthyl. (Methplumbäthylchlorür-Platinchlorid, p. 298.) Pt.

J. prakt. Chem. 81 (1860), 287.

1860: 10. J. W. MALLET. On osmious acid and the position of osmium in the list of elements. Os.

Amer. J. Sci. [2], 29 (1860), 49; Phil. Mag. [4], 19 (1860), 293; Chem. News, 1 (1860), 206; Rép. chim. pur. 2 (1860), 209; Jsb. Chem. 1860, 213.

1860: 11. A. W. HOFMANN. Contributions to the history of the phosphorus-bases. (Analyses of chloroplatinates of phosphorus-bases.) Pt.

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- 1860: 14. C. A. MARTIUS. Ueber die Cyanverbindungen der Platinmetalle. (Inaug. Diss.) Göttingen, 1860. Pt, Pd, Ir, Os, Rh, Ru.  
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- 1860: 15. A. H. CHURCH and E. OWEN. On cespitine and other bases produced by the destructive distillation of peat. (Platinum cespityl ammonium.) Pt.  
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- 1860: 16. G. VON RATH. Krystallographische Beiträge. Kaliumplatinosquesquicyanür,  $2(\text{KaCy}) + \text{Pt}_2\text{Cy}_3 + 5\text{Aq.}$  Pt.  
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- 1860: 17. W. CROSSLEY. On the melting points of some of the elements. (Relation between the melting point and atomic volume of platinum and palladium.) Pt, Pd.  
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- 1860: 18. DELANUE. Entdeckung hämmerbar Platins. Pt.  
J. des Mines, 1860, 548; Berg u. Hütten Ztg. 20 (1861), 335.
- 1860: 19. O. L. ERDMANN. Ueber die Reinigung der Platintiegel, und das Verhalten derselben in der Gasflamme. Pt.  
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- 1860: 22. J. NICKLÈS. Letter on new alloys of platinum (by H. St. C. Deville and H. Debray). Pt, Ir, Os.  
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- 1861: 3. É. GUEYMARD. Notice sur le dosage du platine qui se trouve à l'état de diffusion dans les gîtes métalliques ou dans les roches des Alpes du Dauphiné et de la Savoie. Pt.  
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- 1861: 4. A. A. DAMOUR. Note sur la présence du platine et de l'étain métallique dans les terrains aurifères de la Guyane. Pt.  
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- 1861: 6. W. GIBBS. Researches on the platinum metals. (Chiefly on separation of the metals; review of history and proposal of new method with nitrites.) ("Reprinted from the Contributions to Knowledge of the Smithsonian Institution, vol. 12"; not, however, so published.) Pt, Pd, Ir, Os, Rh, Ru.  
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- 1861: 7. G. KIRCHHOFF and R. W. BUNSEN. Chemische Analyse durch Spectralbeobachtungen. (Solubility of rubidium and cesium platinichlorids, p. 352, 371.) Pt.  
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- 1861: 10. J. LANG. Bidrag till Kännedomen om Platinachlorurens dubbelföreningar. (Platinum double chlorids.) Pt.  
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- 1861: 11. E. BAUDRIMONT. Action exercée par le perchlorure de phosphore sur plusieurs éléments chimiques. (Action of phosphorus pentachlorid on platinum.) Pt.  
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- 1861: 12. L. T. LANGE. Ueber einige neue Cerverbindungen. (Cerium platinecyanür, p. 144.) Pt.  
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- 1861: 13. J. NICKLÈS. Sur les combinaisons formées par les bromures métalliques avec l'éther. (Platinum and palladium bromid with ether.) Pt, Pd.  
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- 1861: 14. P. GRIESS and C. A. MARTIUS. Note sur l'éthylène-chlorure de platine. Pt.  
C. R. 53 (1861), 922; Ann. Chem. (Liebig), 120 (1861), 324; J. prakt. Chem. 86 (1862), 427; Chem. Centrbl. 1862, 773; Rép. chim. pur. 4 (1862), 112.
- 1861: 15. P. T. CLEVE. Om några ammoniakaliska Chromföreningar. (Platinum chlorids of chromium bases.) Pt.  
Oefversigt. Akad. Förhandl. Stockholm, 18 (1861), 163.
- 1861: 16. A. BÉCHAMP and C. SAINT PIÈRE. Recherches sur la séparation (par voie humide) de l'or et du platine, d'avec l'étain et l'antimoine. Réduction du perchlorure du fer par le platine. Pt.  
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- 1861: 18. C. SAINT-PIÈRE. Reponse à M. Faget. (Reduction of ferric chlorid by platinum.) Pt.  
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- 1861: 19. E. SAINT-EDME. Sur la faculté qu'a le platine rendu incandescent par un courant électrique de produire des combinaisons gazeuses. Pt.  
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- 1861: 22. V. REGNAULT. Sur le chaleur spécifique. (Métaux qui accompagnent le platine, p. 13.) Pt, Os, Rh, Ir.  
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- 1861: 23. G. KIRCHHOFF. Untersuchung über das Sonnenspectrum und die Spectren der chemischen Elemente. Pt, Pd, Ir, Os, Rh, Ru.  
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- 1862: 2. C. F. CHANDLER. A new metal in the native platinum of Rogue River, Oregon. —Pt.  
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- 1862: 3. H. VON JOSSA. Ueber die Erzeugnisse der unter der Aufsicht des uralischen Oberbergamtes stehenden Privat Berg- und Hüttenwerke des Uralgebirges im Jahre 1859. Pt.  
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Hüttenwerke für das Jahr 1859. Pt.  
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- 1862: 10. C. CLAUS. Ueber ein allgemeines Verfahren, die einzelnen  
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- 1862: 11. E. BAUDRIMONT. Recherches sur les combinaisons du per-  
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(1863), 380; Rép. chim. pur. 4 (1862), 252; Rép. chim. appl. 4

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- 1862: 17. E. BECQUEREL. Recherches sur la détermination des hautes températures et l'irradiation des corps incandescents. (Fusion of platinum and palladium, Ann. chim. phys., 68 : 136; porosity of platinum in pyrometer.) Pt, Pd.  
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- 1862: 18. H. SAINTE-CLAIRE DEVILLE and H. DEBRAY. Platine aggloméré par voie de fusion. Pt.  
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- 1862: 19. J. P. JOULE. On some amalgams. (Platinum amalgams, p. 122.) Pt.  
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- 1863: 9. H. SAINTE-CLAIRE DEVILLE and L. TROOST. De la mesure des températures élevées. (Porosity of platinum at high temperatures.) Pt, Pd.  
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- 1863: 13. C. A. GRUEL. Die Schweissbarkeit des Platins und ihr Nutzen in der physikalischen Technik. Pt.  
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- 1864: 9. W. CROOKES. On thallium. (Thallium platinichlorid; alloy of thallium and platinum, p. 147.) Pt.  
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- 1873: 13. O. PETERSSON. Untersuchungen über Molecularvolumina einiger Reihen von isomorphen Salzen. (Double salts of platinum.) Pt.  
Nov. Act. Soc. Upsala [3], 9 (1873); Ber. 7 (1874), 478.
- 1873: 14. H. SAINTE-CLAIRE DEVILLE and H. DEBRAY. (Alliage du platine et de l'iridium.) Pt, Ir.  
N. arch. sci. phys. nat. 48 (1873), 45; Jsb. Chem. 1872, 291; Gazz. chim. ital. 4 (1874), 167.
- 1873: 15. S. BOTTONE. Relation zwischen Atomgewicht, specifischem Gewicht, und Härte metallischer Elemente. Pt, Pd.  
Ann. der Phys. (Pogg.), 150 (1873), 644; Chem. Centrbl. 1874, 114; Chem. News, 27 (1873), 215; Amer. J. Sci. [3], 6 (1873), 457; Les Mondes, 31 (1873), 720.
- 1873: 16. F. ŠTOLBA. Ueber Platinschmelztiegel. Pt.  
Sitzber. böhm. Gesel. Wiss. 1873, 325; Chem. Centrbl. 1874, 114; Ztsch. anal. Chem. 13 (1874), 309; J. Chem. Soc. 27 (1874), 1011.
- 1873: 17. F. MOHR. Correction des Platintiegelgewichts. Pt.  
Ztsch. anal. Chem. 12 (1873), 150; Chem. News, 29 (1874), 27; Amer. Chemist, 4 (1873), 233.
- 1873: 18. HÉLONIS. Platinbronce. (Patent.) Pt.  
Ber. 6 (1873), 42; Bul. soc. chim. [2], 19 (1873), 43; Amer. Chemist, 4 (1873), 235; La Gaceta Indust. No. 371; J. Russ. chem. soc. 5, ii (1873), 268; Deutsch. Indust. Ztg. 14 (1873), No. 1; Chem. tech. Mitth. (Elsner), 22 (1872-73), 221.
- 1873: 19. J. B. A. DODÉ. Platinage aurifère des glaces. Pt.  
Bul. soc. chim. [2], 19 (1873), 572; Ber. 6 (1873), 1273; Deutsch. Gewerb. Ztg. 39 (1874), No. 4; Chem. tech. Mitth. (Elsner), 23 (1873-74), 204; Deutsch. Indust. Ztg. 14 (1873), No. 49; Polytechn. Centrbl. 39 (1873), 1440; Polytechn. J. (Dingl.), 211 (1874), 74; J. Chem. Soc. 27 (1874), 928.

- 1873: 20. W. C. RÖNTGEN. Ueber das Löthen von platinirten Gläsern. Pt.  
Ann. der Phys. (Pogg.), 150 (1873), 331; Chem. News, 30 (1874), 187; Chem. tech. Mitth. (Elsner), 24 (1874-75), 128; Repert. für exp. Physik. 10, No. 3; Deutsch. Indust. Ztg. 15 (1874), 328.
- 1873: 21. A. MERGET. Recherches photochimiques sur l'emploi des gaz comme révélateurs, et sur l'influence des conditions physiques au point de vue de la sensibilisation. (Reduction of platinum salts by hydrogen.) Pt, Pd, Ir.  
C. R. 76 (1873), 1470; 77 (1873), 38; Chem. News, 28 (1873), 70.
- 1873: 22. H. PELLET. [Reduction des sels du platine par l'hydrogène.] (Not reduced; reply to Merget, C. R. 77 : 38.) Pt.  
C. R. 77 (1873), 112; Bul. soc. chim. [2], 20 (1873), 258; Chem. Centrbl. 1873; Gaz. chim. 4 (1874), 93; Jsb. Chem. 1873, 291.
- 1873: 23. C. GOURDON. Nouvelles observations concernant l'influence des dépôts métalliques sur le zinc mis en presence des acides et des alcalis; nouveaux procédés d'héliogravure. (Effect of platinum on solution of zinc.) Pt.  
C. R. Assoc. Franç. 2 (1873), 302; C. R. 76 (1873), 1250; Ber. 6 (1873), 680.
- 1873: 24. C. A. GRÜEL. Bedingungen zur sicheren Zündung der Döbereinschen Platin-Feuerzeuge. Pt.  
Indust. Blätter, 10 (1873), 425; Polyt. Notizbl. 28 (1873), 30; Chem. Centrbl. 1874, 119; J. Chem. Soc. 27 (1874), 929; Polyt. J. (Dingler), 211 (1874), 243.
- 1873: 25. R. BÖTTGER. Vorlesungsversuche mit activem Wasserstoff und Sauerstoff. Pd.  
Tagebl. Naturf. Versamml. 1873, 106; Chem. Centrbl. 1873, 818.
- 1873: 26. R. BÖTTGER. Ueber Aufbewahrung und Eigenschaften eines auf elektrolytischem Wege mit Wasserstoff übersättigten Palladiumbleches. Pd.  
Ann. der Phys. (Pogg.), Jubelbd. (1874), 150; J. prakt. Chem. [2], 9 (1874), 193; Chem. Centrbl. 1874, 226; Gaz. chim. 4 (1874), 570; J. Chem. Soc. 27 (1874), 866, 1139; N. arch. sci. phys. nat. 51 (1874), 185; Phil. Mag. [4], 49 (1875), 80; Jsb. Chem. 1874, 295; Amer. Chemist, 5 (1874), 138; 5 (1875), 425.
- 1873: 27. J. J. COQUILLION. Action du platine et du palladium sur les hydrocarbures. Pt, Pd.  
C. R. 77 (1873), 444; Ber. 6 (1873), 1264; Bul. soc. chim. [2], 20 (1873), 493; Chem. Centrbl. 1873, 611; Chem. News, 28 (1873), 125; J. Chem. Soc. 26 (1873), 1214; J. Russ. Chem. Soc. 6, ii (1874), 28.

- 1873: 28. A. VOLLER. Ueber Aenderungen der elektromotorischen Kraft galvanischer Combinationen durch die Wärme (Platin in Salpetersäure). (Inaug. Diss.) Pt.  
Ann. der Phys. (Pogg.), 149 (1873), 394; Jsb. Chem. 1873, 122.
- 1873: 29. P. A. FAVRE. Recherches thermiques sur la condensation des gaz par les corps solides. Absorption de l'hydrogène par le noir de platine. Pt.  
C. R. 77 (1873), 649; Chem. News, 28 (1873), 213; J. Chem. Soc. 27 (1874), 15.
- 1873: 30. H. SCHRÖDER. Dichtigkeitsmessungen, Heidelberg, 1873. (Density of potassium and ammonium chloroplatinates.) Pt.  
Jsb. Chem. 1879, 32.
- 1874: 1. H. J. BURKART. Ueber neue mexicanische Fundorte einiger Mineralien. (Occurrence of platinum in Mexico, p. 594.) Pt.  
Neues Jahrb. Mineral. 1874, 587; Dingl. pol. J. 240 (1881), 213; Jsb. Chem. 1874, 1230; J. Chem. Soc. 28 (1875), 551.
- 1874: 2. A. FRENZEL. Mineralogisches [S. Eisenplatin]. (From Russia, p. 684.) Pt.  
Neues Jahrb. Mineral. 1874, 673; Jsb. Chem. 1874, 1230.
- 1874: 3. H. MORIN. L'un lingot de 250 kilogrammes de platine et d'iridium alliés, fondu, etc. (Properties of alloy.) Pt, Ir.  
C. R. 78 (1874), 1502; Dingl. pol. J. 213 (1874), 337; Jsb. Chem. 1874, 1065; J. Russ. Chem. Soc. 6, ii (1874), 298; Polyt. Centrbl. 40 (1874), 966; Amer. Chemist, 5 (1874), 146.
- 1874: 4. F. BEILSTEIN. Die chemische Grossindustrie auf der Weltausstellung zu Wien, 1873. (Platinum manufactory of Johnson, Matthey and Co.) Pt, Pd, Ir, Rh, Os, Ru.  
Polyt. J. (Dingler), 211 (1874), 155; Chem. Centrbl. 1874, 176; Jsb. Chem. 1874, 1064.
- 1874: 5. ———. Production of platinum. Pt.  
Amer. Chemist, 4 (1874), 440; from Engineering.
- 1874: 6. H. SAINT-CLAIRE DEVILLE, H. DEBRAY and H. MORIN. (Separation of iridium from platinum ores, platinum-iridium alloys, and normal metal; also poisonous qualities of osmium.) Pt, Ir, Os.  
Technologiste, 36 (1874), 194; Chem. Centrbl. 1874, 609; Polyt. Centrbl. 40 (1874), 966.
- 1874: 7. L. J. TROOST and P. HAUTEFEUILLE. Note sur le palladium hydrogène. Densité de l'hydrogène combiné avec métaux. Pd.  
C. R. 78 (1874), 686, 968; Ann. chim. phys. [5], 2 (1874), 279, 287; Bul. soc. chim. [2], 22 (1874), 118, 120; Ann. der Phys. (Pogg.),

- 153 (1874), 144; Ber. 7 (1874), 480; Chem. Centrbl. 1874, 276; Chem. News, 29 (1874), 196; J. Chem. Soc. 27 (1874), 660; J. prakt. Chem. [2], 9 (1874), 199; Phil. Mag. [4], 47 (1874), 397; Jsb. Chem. 1874, 293; J. Russ. Chem. Soc. 6, ii (1874), 165; Amer. Chem. 5 (1874), 143.
- 1874: 8. J. MOUTIER. Sur la chaleur dégagée par la combinaison de l'hydrogène avec les métaux. Pd.  
C. R. 79 (1874), 1242; Chem. Centrbl. 1875, 138; l'Institut, 42 (1874), 412; Jsb. Chem. 1874, 112.
- 1874: 9. P. A. FAVRE. Recherches sur l'hydrogène. (Heat development of platinum-hydrogen and palladium-hydrogen.) Pt, Pd.  
C. R. 78 (1874), 1257; Ber. 7 (1874), 737; Jsb. Chem. 1874, 111; Bul. soc. chim. [2], 22 (1874), 486.
- 1874: 10. P. A. FAVRE. Recherches thermiques sur la condensation des gas par les corps solides et la chaleur dégagée dans l'acte de cette absorption. (Condensation of hydrogen by platinum and palladium, p. 215, 227, 256.) Pt, Pd.  
Ann. chim. phys. [5], 1 (1874), 209.
- 1874: 11. J. L. SMITH. Condensation of air on the surface of platinum. Pt.  
Amer. Chemist, 5 (1874), 212; Chem. News, 31 (1875), 55; J. Chem. Soc. 28 (1875), 480.
- 1874: 12. J. L. SMITH. A ready method of showing the absorption of hydrogen by palladium. Pd.  
Amer. Chemist, 5 (1874), 213; Chem. News, 31 (1875), 56; Jsb. Chem. 1874, 177; J. Chem. Soc. 28 (1875), 424.
- 1874: 13. J. THOMSEN. Beryllium-Platinchlorid. Pt.  
Ber. 7 (1874), 75; Chem. Centrbl. 1874, 245.
- 1874: 14. A. WELKOW. Beryllium-Palladiumchlorid. Pd.  
Ber. 7 (1874), 38; Bul. soc. chim. [2], 21 (1874), 273; Chem. Centrbl. 1874, 245; Chem. News, 29 (1874), 155; Gaz. chim. 4 (1874), 278.
- 1874: 15. A. WELKOW. Beryllium-Palladiumchlorür. Pd.  
Ber. 7 (1874), 803; Bul. soc. chim. [2], 22 (1874), 499; Chem. Centrbl. 1874, 467; Gaz. chim. 5 (1875), 61.
- 1874: 16. A. WELKOW. Aluminium-Platinchlorid. Pt.  
Ber. 7 (1874), 304; Bul. soc. chim. [2], 22 (1874), 153; Chem. Centrbl. 1874, 292; Gaz. chim. 4 (1874), 302.
- 1874: 17. A. WELKOW. Aluminium-Palladiumchlorür. Pd.  
Ber. 7 (1874), 802; Bul. soc. chim. [2], 22 (1874), 499; Chem. Centrbl. 1874, 467; Chem. News, 29 (1874), 265; Gaz. chim. 5 (1875), 61; J. Russ. Chem. Soc. 6, ii (1874), 313.

- 1874: 18. P. T. CLEVE. Bidrag till jordmetallernas kemi. (Chlorids and cyanids of platinum and thorium, No. 6; lanthanum, 7; didymium, 8; yttrium, 12; erbium, 12.) Pt.  
Bihang. Akad. Handl. (Stockholm), 2 (1874), 6, 7, 8, 12; Bul. soc. chim. [2], 21 (1874), 115, 196, 246, 344; Ber. 8 (1875), 128.
- 1874: 19. [F. WÖHLER.] Palladiumoxydul in Wasserstoffgas. Pd.  
Nachrichten, Göttingen, 1874, 420; Ann. Chem. (Liebig), 174 (1874), 60; Bul. soc. chim. [2], 23 (1875), 267; Gaz. chim. 6 (1876), 213; Chem. Centrbl. 1874, 770; Jsb. Chem. 1874, 295; Ztsch. ges. Wiss. 11 (1875), 68; Amer. Chemist, 5 (1875), 384; J. Russ. Chem. Soc. 7, ii (1875), 8.
- 1874: 20. [F. WÖHLER.] Notiz über ein Palladiumsalz. (Sodium palladium sulfite.) Pd.  
Nachrichten, Göttingen, 1874, 419; Ann. Chem. (Liebig), 174 (1874), 199; Bull. soc. chim. [2], 23 (1875), 267; Chem. Centrbl. 1874, 803; Chem. News, 30 (1874), 275; Gaz. chim. 6 (1876), 224; Jsb. Chem. 1874, 296; Ztsch. ges. Wiss. 11 (1875), 67; Amer. Chemist, 5 (1875), 353; J. Chem. Soc. 28 (1875), 134.
- 1874: 21. W. SKEY. On the formation of certain double metallic sulphocyanides (of platinum with anilin). Pt.  
Chem. News, 30 (1874), 33; Ber. 7 (1874), 1459; Jsb. Chem. 1874, 300.
- 1874: 22. W. SKEY. Notes upon the production of certain double salts of the aniline bases and indigo with metallic salts (with platinum chlorid and thiocyanate). Pt.  
Chem. News, 30 (1874), 33; Ber. 7 (1874), 1459; Jsb. Chem. 1874, 300.
- 1874: 23. R. SCHNEIDER. Ueber neue Schwefelsalze. (Summary.) Pt, Pd.  
Ann. der Phys. (Pogg.), 153 (1874), 588; J. prakt. Chem. [2], 11 (1875), 91; J. Chem. Soc. 28 (1875), 533.
- 1874: 24. S. JOLIN. Om cerium och dess föreningar. (Double chlorids and cyanids of platinum and cerium.)  
Bihang. Akad. Handl. 2 (1874), 14; Bul. soc. chim. [2], 21 (1874), 533.
- 1874: 25. F. GRAMP. Ueber Affinitätsverhältnisse der Halogenmetallverbindungen. (Platinum and palladium.) Pt, Pd.  
Ber. 7 (1874), 1723; J. Chem. Soc. 28 (1875), 423; Jsb. Chem. 1874, 49.
- 1874: 26. G. KRAUSE. Beitrag zur Bestimmung des Kalium als Kaliumplatinchlorid. Pt.  
Arch. für Pharm. 205 (1874), 407; Ztsch. anal. Chem. 14 (1875), 184; Pharm. Journ. 5 (1875), 782; Jsb. Chem. 1874, 978; Amer. Chemist, 6 (1876), 437.

- 1874: 27. H. SAINTE-CLAIRE DEVILLE and H. DEBRAY. Sur une propriété nouvelle du rhodium métallique. (Reduction of formic acid.) Rh. Pt, Pd, Ir, Ru.  
C. R. 78 (1874), 1782; Bul. soc. chim. [2], 22 (1874), 360; Ber. 7 (1874), 1038; Chem. Centrbl. 1874, 513; Chem. News, 30 (1874), 98; J. Chem. Soc. 27 (1874), 1076; Jsb. Chem. 1874, 296; J. Russ. Chem. Soc. 6, ii (1874), 301.
- 1874: 28. H. SAINTE-CLAIRE DEVILLE. [Poisonous qualities of osmic acid.] Os.  
C. R. 78 (1874), 1509; Chem. Centrbl. 1874, 610.
- 1874: 29. G. VULPIUS. Ueber Platinreduction. (Preparation of platinum sponge.) Pt.  
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- 1874: 30. C. A. WINKLER. Ueber die Löslichkeit des legirten Platins in Salpetersäure. (When alloyed with silver, copper, lead, bismuth, or zinc.) Pt.  
Ztsch. anal. Chem. 13 (1874), 369; Chem. Centrbl. 1875, 162; J. Chem. Soc. 13 (1875), 428; Berg u. Hütten Ztg. 34 (1875), 145; J. Russ. Chem. Soc. 7, ii (1875), 27; Amer. Chemist, 5 (1875), 402.
- 1874: 31. H. TOPSÖE. Beiträge zur krystallographischen Kenntniss der Salze der seltenen Erdmetalle. (Double platinum chlorids and cyanids.) Pt.  
Bihand. Akad. Handl. (Stockholm), 2 (1874), 5; Ber. 8 (1875), 129.
- 1874: 32. A. H. L. FIZEAU. Dilatation du alliage platine-iridium. Ir, Pt.  
C. R. 78 (1874), 1205; Jsb. Chem. 1874, 70.
- 1874: 33. J. L. SMITH. Gold-lined capsules and crucibles. Pt.  
Amer. Chemist, 5 (1874), 213; Chem. News, 31 (1875), 55; Dingl. pol. J. 219 (1876), 183; Jsb. Chem. 1876, 1096; Chem. tech. Mitth. (Elsner), 25 (1875-76), 203; Ztsch. anal. Chem. 14 (1875), 329.
- 1874: 34. H. CARMICHAEL. (Platinum digester.) Pt.  
Proc. Amer. Assoc. 1874; Amer. Chemist, 5 (1874), 163.
- 1874: 35. E. REICHARDT. Brüchiges Platin. (With silicon.) Pt.  
Arch. für Pharm. 205 (1874), 123; Chem. Centrbl. 1874, 595; Dingl. pol. J. 213 (1874), 445; 240 (1881), 217; Jsb. Chem. 1874, 294; Amer. Chemist, 6 (1875), 155.
- 1874: 36. A. POLAIN. De la résistance du bronzephosphoreux et de ses applications dans l'industrie. (Plating phosphorbronze with platinum.) Pt.  
Rev. Univ. des Mines, 35 (1874), 595; Dingl. pol. J. 217 (1875), 494.



- 1874: 37. P. DE WILDE. Action de l'hydrogène sur l'acétylène et l'éthylène sous l'influence du noir de platine. Pt.  
Bul. Acad. Sci. Bruxelles, 37 (1874), 73; Ber. 7 (1874), 353; Bul. soc. chim. [2], 21 (1874), 446; J. Chem. Soc. 27 (1874), 882.
- 1874: 38. R. C. BÖTTGER. Ueber Aufbewahrung und Eigenschaften eines auf elektrolytischem Wege mit Wasserstoff übersättigten Palladiumbleches. Pd.  
J. prakt. Chem. 9 (1874), 193; Tageblatt Naturf. Versamml. 1875, 54; Chem. Centrbl. 1875, 643; J. Russ. Chém. Soc. 7, ii (1875), 97.
- 1874: 39. M. TRAUBE. Zur Theorie der Fermentwirkung. (Platinum black on sugar.) Pt.  
Ber. 7 (1874), 115; Ztsch. anal. Chem. 13 (1874), 349; N. arch. sci. phys. nat. 49 (1874), 141; Jsb. Chem. 1874, 951.
- 1874: 40. E. HAGENBACH-BISCHOFF. Fernere Versuche über Fluorescenz. (Of platinocyanids, p. 309.) Pt.  
Ann. der Phys. (Pogg.), Jubelb. (1874), 303; Jsb. Chem. 1874, 155.
- 1874: 41. H. TOPSÖE. Krystallographisch-chemische Untersuchungen (über Baryumplatinchlorid und Natriumplatinumbromid). Pt.  
Sitzber. Wien. Acad. 69, ii (1874), 261; Jsb. Chem. 1874, 179.
- 1874: 42. WILLIS, JR. (Platinum and iridium in photography.) Pt, Ir.  
Polyt. Notizbl. (1874), No. 6; Amer. Chemist, 5 (1874), 153; Chem. Centrbl. 1874, 583; J. Chem. Soc. 27 (1874), 1019.
- 1874: 43. D. MACALUSO. Untersuchung über die galvanische Polarisation durch Chlor und Wasserstoff. Ueber die electromotorische Kraft des mit kleinen Mengen von Chlor beladenen Platins. Pt.  
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- 1875: 1. A. DESCLOIZEAU. Note sur l'élément pyroxénique de la roche associée au platine de l'Oural. Pt.  
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- 1875: 2. G. A. DAUBRÉE. Association, dans l'Oural, du platine natif à la roches à base de péridot; relation d'origine qui unit ce métal avec le fer chromé. (Matrix of platinum.) Pt.  
C. R. 80 (1875), 707; Bul. Géol. Soc. (Paris), 3 (1875), 311; Neues Jahrb. Mineral. 1875, 540; Jsb. Chem. 1875, 1194; Ann. des Mines [7], 9 (1876), 123; Amer. Chemist, 6 (1876), 469; Le Technol. 1876, No. 7.
- 1875: 3. H. SAINTE-CLAIRE DEVILLE. Sur les alliages de platine et de fer. (Rejoinder to Daubrée, 1875: 27.) Pt, Ir.  
C. R. 80 (1875), 589; Chem. News, 31 (1875), 171; J. Chem. Soc. 28 (1875), 534; Jsb. Chem. 1875, 232, 1196; 1880, 362; Monit. scientif. [3], 6 (1876), 548; Chem. Industrie, 3 (1880), 22.

- 1875: 4. K. L. F. VON SANDBERGER. [Barytglimmer vom Habachtal; Brauneisenerz-Pseudomorphosen, welche Platin enthalten, aus Mexico.] Pt.  
Neues Jahrb. Mineral. 1875, 625; J. Chem. Soc. 29 (1876), 54; Jsb. Chem. 1875, 1194.
- 1875: 5. ————. Werth von Metallen. Pt, Pd, Ir, Rh, Os, Ru.  
Berg und Hütten Ztg. 34 (1875), 244 (from Mining and Sci. Press); Chem. Centrbl. 1875, 544.
- 1875: 6. ————. Zur Industrie der Edelmetalle. (Scheidung der alten Thaler in Frankfurt a. M.) Pt, Pd.  
Indust. Blätter, 12 (1875), 386; Dingl. pol. J. 218 (1875), 376.
- 1875: 7. ————. (Apparatus at Conservatory of Arts and Measures [Paris] for fusion of platinum.) Pt.  
Amer. Chemist, 5 (1875), 354; from La Nature.
- 1875: 8. ————. (Forging of a platinum ingot.) Pt.  
Amer. Chemist, 5 (1875), 394; from La Nature.
- 1875: 9. J. R. VON WAGNER. Ueber die Verwendbarkeit des Broms in der Hydrometallurgie, der Probirkunst, und der chemischen Technologie. (Extraction of platinum.) Pt.  
Chem. Centrbl. 1875; Dingl. pol. J. 218 (1875), 254; Bul. soc. chim. [2], 25 (1876), 138.
- 1875: 10. J. L. SMITH. A convenient instrument for showing the absorption of hydrogen gas by palladium. (Read at A. A. A. S., 1875.) Pd, Pt.  
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- 1875: 11. L. H. LAUDY. The occlusion of hydrogen by palladium. Pd.  
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- 1875: 12. L. TROOST and P. HAUTEFEUILLE. Sur la dissolution de l'hydrogène dans les métaux. Pd.  
C. R. 80 (1875), 788; Chem. News, 31 (1875), 196.
- 1875: 13. R. GODEFFROY. Einige neue Salze und Reactionen des Caesiums und Rubidiums. (Double platinum chlorids.) Pt.  
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- 1875: 14. A. VON LASAULX. Ueber die Krystallformen des Natriumiridium- und des Natriumrhodium-Sesquichlorürs. Ir, Rh.  
Neues Jahrb. Min. 1875, 128.

- 1875: 15. B. DELACHANAL and A. MERMET. Sur une composé de platine, d'étain et d'oxygène, analogue au pourpre de Cassius. (Oxyde platinostannique de M. Dumas.) Pt.  
C. R. 81 (1875), 370; Bul. soc. chim. [2], 24 (1875), 435; Ber. 8 (1875), 1353; Chem. Centrbl. 1875, 625; Chem. News, 32 (1875), 157; Gaz. chim. 6 (1876), 159; J. Chem. Soc. 29 (1876), 48; Jsb. Chem. 1875, 232; J. Russ. Chem. Soc. 7, ii (1875), 404; Amer. Chemist, 6 (1876), 319.
- 1875: 16. S. KERN. On the action of sulphocyanides on palladium chloride and nitrate. (No precipitate.) Pd.  
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- 1875: 17. S. KERN. On some reactions of iodine and palladium chloride with potassium ferrocyanide. Pd.  
Chem. News, 33 (1876), 184; J. Russ. Chem. Soc. 7, i (1875), 316; J. Chem. Soc. 30 (1876), 325.
- 1875: 18. H. SAINTE-CLAIRE DEVILLE and H. DEBRAY. Du ruthenium et de ses composés oxygénés. Ru.  
C. R. 80 (1875), 457; Ann. chim. phys. [5], 4 (1875), 537; Bul. soc. chim. [2], 24 (1875), 191; Ber. 8 (1875), 339; Chem. Centrbl. 1875, 258; J. Chem. Soc. 29 (1876), 48; Jsb. Chem. 1875, 233; Amer. Chemist, 6 (1875), 189; 6 (1876), 396; Gazz. chim. ital. 6 (1876), 518.
- 1875: 19. A. ATTERBERG. Sur quelques combinaisons du glucinium (platinocyanid). Pt.  
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- 1875: 20. V. A. VIDAÜ. Note sur les cuprocyanures et le pallado-cyanure de potassium. Pd.  
J. de pharm. 22 (1875), 321; Amer. Chemist, 6 (1876), 319; Gazz. chim. ital. 6 (1876), 224; J. Chem. Soc. 31 (1877), 456.
- 1875: 21. F. SELMI (and C. BETTELLI). Nuovi reattivi per riconoscere e discernere gli alcaloidi venefici. (Potassium iodoplatinate as a reagent for the alkaloids.) Pt.  
Mem. Accad. Sci. Bologna, 6 (1875), 189, 201; Rendiconti. Accad. Sci. Bologna, 1875, 104, 153; Gaz. chim. 5 (1875), 255; J. Chem. Soc. 29 (1876), 113, 114; Ber. 8 (1875), 1198; 9 (1876), 196; Bul. med. d. Bologna, 19, 321.
- 1875: 22. H. ZENGER. Eine bis jetzt vernachlässigte Iodquelle. (Süßwasserpflanzen.) (Detection of iodine by palladium iodid.) Pd.  
Arch. für Pharm. 206 (1875), 137; J. Chem. Soc. 29 (1876), 876; Amer. Chemist, 6 (1876), 259; Ztsch. anal. Chem. 14 (1875), 368.

- 1875: 23. W. C. LOSSEN. Notiz über die reducirende Wirkung des Hydroxylamins (auf Platinchlorid). Pt.  
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- 1875: 24. V. MEYER and J. LOCHER. Ueber die Einwirkung der Säuren auf nitrirte Fettkörper. (Action of hydrogen on hydroxylamin in presence of platinum tetrachlorid.) Pt.  
Ber. 8 (1875), 219 (foot-note).
- 1875: 25. T. J. FAIRLEY. On new solvents for gold, silver, platinum, &c., with an explanation of the so-called catalytic action of these metals and their salts on hydrogen dioxide (dioxid). Pt.  
Brit. Assoc. Rep. 45 (1875), 42 (title only); Ber. 8 (1875), 1600.
- 1875: 26. H. SAINTE-CLAIRE DEVILLE and H. DEBRAY. De la densité du platine et de l'iridium purs, et de leur alliages. Pt, Ir.  
C. R. 81 (1875), 829; Bul. soc. chim. [2], 26 (1876), 157; Ber. 8 (1875), 1591; Chem. Centrbl. 1876, 4; Chem. News, 32 (1875), 281; Amer. J. Sci. [3], 11 (1876), 142; Monit. scient. [3], 6 (1876), 75; Phil. Mag. [4], 50 (1875), 558; J. Chem. Soc. 29 (1876), 523; Ztsch. anal. Chem. 15 (1876), 451; Jsb. Chem. 1875, 231; J. Russ. Chem. Soc. 8, ii (1876), 109; Amer. Chemist, 6 (1876), 398; J. de pharm. 23 (1876), 168; Gazz. chim. ital. 6 (1876), 475.
- 1875: 27. G. A. DAUBRÉE. Expériences sur l'imitation artificielle du platine natif magnétipolaire. Pt.  
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- 1875: 28. A. SCHEURER-KESTNER. Dissolution du platine dans l'acide sulfurique, pendant l'opération industrielle de la concentration. Pt.  
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- 1875: 29. A. BAUER. Ueber die Einwirkung von Schwefelsäure auf Blei. (And lead platinum alloys.) Pt.  
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- 1875: 30. P. WEISKOPF. Kupferlegirung und Silber intensiv schwarz zu färben. (Durch Platinchlorür.) Pt.  
Dingl. pol. J. 215 (1875), 470.
- 1875: 31. HEYL. [Pflug's Platinfarbe.] Pt.  
Gewerbeblatt f. Grossh. Hessen, 38 (1875), 229; Polyt. Notizbl. 30 (1875), 267; Chem. Centrbl. 1875, 710; Amer. Chemist, 6 (1875), 236.

- 1875: 32. J. J. COQUILLION. Sur l'action du platine et du palladium sur les hydrocarbures de la série benzénique. (Oxidation.) Pt, Pd. C. R. 80 (1875), 1089; Ber. 8 (1875), 697; Chem. News, 31 (1875), 239; J. Chem. Soc. 28 (1875), 1188.
- 1875: 33. P. CHAMPION, H. PELLET, and GRENIER. Application de l'électricité à l'inflammation des fourneaux de mine, torpilles, etc., et à l'industrie minière. (Amorces à fils de platine, p. 84.) Pt. Ann. chim. phys. [5], 5 (1875), 28.
- 1876: 1. A. TERREIL. Analyse du platine natif magnétique de Nischne-Tagilsk. Pt. Bul. soc. chim. [2], 25 (1876), 482; C. R. 82 (1876), 1116; Ber. 9 (1876), 850; Chem. Centrbl. 1876, 408; Chem. News, 33 (1876), 213; Gaz. chim. 7 (1877), 1116; J. Chem. Soc. 30 (1876), 386; Jsb. Chem. 1876, 290, 1218.
- 1876: 2. G. A. DAUBRÉE. Presence du nickel dans le platine natif. C. R. 82 (1876), 1116; Jsb. Chem. 1876, 290. Pt.
- 1876: 3. G. VON USLAR. Die Platin und Silber führende Seifen von Santa Maria de las Animas (Mexico). Pt. Berg und Hütten Ztg. 35 (1876), 88; Dingl. pol. J. 240 (1881), 213.
- 1876: 4. H. RÖSSLER. Ueber das Vorkommen von Palladium, Platin und Selen in den Silbermünzen. Pt, Pd. Ann. Chem. (Liebig), 180 (1876), 240; Bul. soc. chim. [2], 27 (1877), 284; Amer. J. Sci. [3], 11 (1876), 486; Jsb. Chem. 1876, 285.
- 1876: 5. FRANTZ. Russlands Montanproduction. Pt. Oberschles. Ztsch. (1876), No. 16; Berg und Hütten Ztg. 35 (1876), 179; Chem. Centrbl. 1876, 384.
- 1876: 6. BRACHELLI. Jährliche Metallproduction. Pt. Berg und Hütten Ztg. 35 (1876), 179 (from Die Staaten Europa's); Chem. Centrbl. 1876, 368.
- 1876: 7. ————. Die Preise aller Metalle. Pt, Pd, Ir, Rh, Os, Ru. Berg und Hütten Ztg. 35 (1876), 410 (from Stummer's Ingenieur); Chem. Centrbl. 1877, 160.
- 1876: 8. ————. Zur Darstellung des Platins. (Editorial review.) Pt. Dingl. pol. J. 220 (1876), 95.
- 1876: 9. J. PHILIPP. Darstellung Platins von Heraeus (auf der Wiener Ausstellung). Pt, Pd, Ir, Rh, Os, Ru. Ämtlicher Ber. über Wiener Ausst. Heft. 20, 999; Dingl. pol. J. 220 (1876), 95; Jsb. Chem. 1876, 1075.

- 1876: 10. E. H. SAINTE-CLAIRE DEVILLE and J. H. DEBRAY. De l'osmium. (Preparation and properties.) Os.  
C. R. 82 (1876), 1076; Ber. 9 (1876), 848; Bull. soc. chim. [2], 26 (1876), 339; Chem. Centrbl. 1876, 417; Chem. News, 33 (1876), 230; Gaz. chim. 7 (1877), 34; J. Chem. Soc. 30 (1876), 279; Ztsch. anal. Chem. 15 (1876), 454; Jsb. Chem. 1876, 301; Amer. Chemist, 7 (1876), 120.
- 1876: 11. E. H. SAINTE-CLAIRE DEVILLE and J. H. DEBRAY. Sur les propriétés physiques et chimiques du ruthenium. (Important memoir on preparation, crystallization, analysis, alloys, and tetroxid.) Ru.  
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- 1876: 12. L. F. NILSON. Zur Frage über die Valenz der seltenen Erdmetalle. (Chlorplatينات of the rare earths, and iron, chromium, indium, aluminum and tin.) Pt.  
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- 1876: 14. A. GUYARD (H. TAMM). Note sur le siliciure de platine. Pt.  
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- 1876: 15. J. B. J. BOUSSINGAULT. Sur la siliciuration du platine et de quelques autres métaux. Pt, Pd, Ru, Ir.  
C. R. 82 (1876), 591; Ann. chim. phys. [5], 8 (1876), 145; Ber. 9 (1876), 503; Bul. soc. chim. [2], 26 (1876), 265; Chem. Centrbl. 1876, 307; Chem. News, 33 (1876), 148; Dingl. pol. J. 225 (1877), 108; Gaz. chim. 6 (1876), 496; J. Chem. Soc. 30 (1876), 47; Jsb. Chem. 1876, 291; J. Russ. Chem. Soc. 8, ii (1876), 392; 9, ii (1877), 207.

- 1876: 16. F. KRÜGER. Ueber Isomerien bei organischen Sulfinverbindungen. (Platinum salts of sulfur bases.) Pt.  
J. prakt. Chem. [2], 14 (1876), 193; Gazz. chim. ital. 7 (1877), 246.
- 1876: 17. W. HEINTZ. Ein neues, zwei verschiedene Ammoniakbasen enthaltendes Platinsalz. (Triacetonamin und Triacetonalkamin.) Pt.  
Ann. Chem. (Liebig), 183 (1876), 317; Bull. soc. chim. [2], 28 (1877), 20; J. Chem. Soc. 31 (1877), 592; Amer. Chemist, 7 (1877), 360.
- 1876: 18. G. QUESNEVILLE. Action de l'ammoniaque et des ammoni-  
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platinique. Pt.  
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- 1876: 19. P. CASAMAJOR. On the amalgamation of iron and of some  
other metals. (Platinum and palladium amalgam.) Pt, Pd.  
Amer. Chemist, 6 (1876), 450; Chem. News, 34 (1876), 34; Engin.  
Mag. 15 (1876), 305; Jsb. Chem. 1876, 281; Archiv Pharm. [3],  
11 (1877), 464; J. Chem. Soc. 34 (1878), 474.
- 1876: 20. G. H. BILLINGS. The properties of iron alloyed with other  
metals. (With platinum, p. 451.) Pt.  
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(1878), 430; Eng. and Min. J. 23 (1877), 415.
- 1876: 21. A. CHATIN. Des causes d'insuccès dans la recherche de  
minimes quantités d'iode. (Detection of iodine by palladium  
chlorid.) Pd.  
C. R. 82 (1876), 128; Ztsch. anal. Chem. 15 (1876), 460.
- 1876: 22. F. BECKER. Ueber einige Tellurverbindungen. (Separation  
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- 1876: 23. M. KRETSCHY. Können die indirecten Methoden der Alkali-  
bestimmung sich gegenseitig controliren oder zu Controle der  
directen Methoden verwendet werden? (Bestimmung des Kalis  
mittelst Chlorplatin, p. 49.) Pt.  
Ztsch. anal. Chem. 15 (1876), 37.
- 1876: 24. S. KERN. On the action of magnesium on some metallic  
salts. (Platinum salts, p. 112; palladium salts, 236.) Pt, Pd.  
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- 1876: 25. S. KERN. On some reactions of iodine and palladium  
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Chem. News, 33 (1876), 184.

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- 1876: 27. F. WÖHLER. Notiz über das Verhalten des Palladiums in der Alkoholflamme. (Decomposition of alcohol and ethylene.) Pt.  
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- 1876: 28. W. SKEY. On the oxidation of silver and platinum by oxygen in the presence of water. Pt.  
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- 1876: 30. J. THOMSEN. Ueber die Neutralization. (Neutralizationswärme der Ammoniumbasen.) Pt.  
J. prakt. Chem. [2], 13 (1876), 241; Chem. Centrbl. 7 (1876), 545; Jsb. Chem. 1876, 83.
- 1876: 31. F. KOPFER. On the use of platinum in the ultimate analysis of chemical compounds. Pt.  
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- 1876: 32. F. KOPFER. Ueber die Anwendung des Platins bei der Elementaranalyse. Pt.  
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- 1876: 33. A. MITSCHERLICH. Elementaranalyse vermitteltst Quecksilberoxyd. (Use of potassium chlorplatinate to determine oxygen directly, p. 374.) Pt.  
Ztsch. anal. Chem. 15 (1876), 371.
- 1876: 34. E. F. DÜRRE. Studien über die Ausnützung der Wärme in den Oefen der Hüttenwesen. (Platinschmelzen in Knallgasgebläse.) Pt.  
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- 1876: 35. C. J. H. W. Platinum combustion tubes. Pt.  
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- 1876: 36. W. D. HERMAN. Platinum combustion tubes. Pt.  
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- 1876: 37. W. JAGO. Rapid filtration (by platinum filters). Pt.  
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- 1876: 38. C. STÖCKMANN. Ueber das Aufschliessen von Silicaten.  
(Getting melt out of platinum crucible.) Pt.  
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- 1876: 39. F. ŠTOLBA. Ueber die Anwendung des Borfluorkaliums als  
Flussmittel bei Löthungen. (Zur Reinigung der Platintiegel  
durch Borfluorkalium und Borsäure.) Pt.  
Sitzber. böhm. Gesel. (Prag), 1876, 220; Ztsch. anal. Chem. 16  
(1877), 95.
- 1876: 40. F. BODE. Faure und Kessler's Platinschale. (Zur Schwefel-  
säureconcentration.) Pt.  
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- 1876: 41. F. BODE. Concentration von Schwefelsäure in Platinschalen  
nach Faure und Kessler. Pt.  
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- 1876: 42. F. BODE (nach SCHEURER-KESTNER). Ueber Abnützung der  
Platingefässe beim Concentration von Schwefelsäure. Pt.  
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- 1876: 44. L. KESSLER (also R. HASENCLEVER and JOHNSON, MATTHEY  
& Co.). Ueber Faure und Kessler's Platinschale. Pt.  
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- 1876: 45. [J. ZEMAN and F. FISCHER.] Ueber Faure und Kessler's  
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- 1876: 46. F. BODE. Neue Formen der alten Platinkessel. Pt.  
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- 1876: 47. LAMY. Appareils à cuvette de platine de MM. Faure et Kess-  
ler pour la concentration d'acide sulfurique. Pt.  
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- 1876: 48. R. C. BÖTTGER. Neues Verfahren Metalle auf galvanischem  
Wege mit Platin zu überziehen. Pt.  
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395; J. Frank. Inst. [3], 76 (1878), 348.

- 1876: 49. A. BERTRAND. Recherches sur la production de dépôts électro-chimiques . . . de palladium. Pd.  
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- 1876: 50. FRANTZ. Application électrochimique du palladium en vue de suppléer l'argenture. (French patent 107961, May 8, 1875.) Pd.  
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- 1876: 51. S. DE LUCA. Sul piombo contenuto in due punte di platino de' parafulmini dell' Osservatorio vesuviano. (Lead in platinum points on lightning rods.) Pt.  
Rendiconti Accad. Napoli, 15 (1876), 69; C. R. 82 (1876), 1187; J. Chem. Soc. 30 (1876), 340; Jsb. Chem. 1876, 290.
- 1876: 52. ————. Untersuchung von Filsinger über die sogenannte Pflug'sche Platinanstrichmasse (Platinfarbe). (Contains no platinum.) Pt.  
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- 1876: 53. J. J. COQUILLION. Procédé pour doser les hydrocarbures et en particulier le grison dans les mines. (Use of palladium wire for ignition.) Pd.  
C. R. 83 (1876), 394; Ber. 10 (1877), 730; Ztsch. anal. Chem. 17 (1878), 329; Jsb. Chem. 1876, 959.
- 1876: 54. J. J. COQUILLION. Sur les limites entre lesquelles peut se produire l'explosion du grison, et sur nouvelles propriétés du palladium. (Combustion without explosion.) Pd.  
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- 1876: 55. M. R. ZDRAWKOWITCH. Préparation du noir de platine au moyen de la glycérine. Pt.  
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- 1876: 56. R. C. BÖTTGER. Palladiumwasserstoff. Pd.  
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- 1876: 59. J. B. DUMAS. Études sur le phylloxera et sur les sulfocarbonates. (Action of platinum sponge on sulfocarbonates, p. 71.)  
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- 1876: 60. L. BLEEKRODE. On electrical conductivity and electrolysis of chemical compounds. (Non-electrolysis of osmium tetroxid.) Os.  
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- 1876: 62. C. G. KNOTT, J. MACGREGOR and C. M. SMITH. The thermo-electric properties of cobalt. (Thermo-electric properties of cobalt-palladium.) Pd.  
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- 1876: 63. A. LALLEMAND. Recherches sur l'illumination des corps transparents. (Polarisation on surface of platinum black, p. 132.)  
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- 1876: 65. G. MATTHEY. Règle en platine iridié de l'Association Géo-désique Internationale (Lettre). Pt, Ir.  
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- 1876: 66. E. H. SAINTE-CLAIRE DEVILLE. Observations sur la communication de M. Matthey (Règle en platine-iridié). Pt, Ir.  
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- 1877: 1. ———. Ueber das weisse Gold oder die Platina del Pinto. Pt.  
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- 1877: 2. S. KERN. On Russian platinum-ore from the Oural Mountains. Pt, Pd, Ir, Rh, Os, Ru.  
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- 1877: 3. S. KERN. On the new metal davyum; note on davyum; on some new researches on the metal davyum; on the spectrum of the metal davyum; solubility of sodium davyum chloride; some remarks on the metal davyum. Da.  
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- 1877: 4. A. H. ALLEN. Contributions on chemical analysis. (Criticism on S. Kern's discovery of davyum.) Da.  
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- 1877: 5. K. KARMARSH. Betrachtungen über die neueren Veränderungen und den gegenwärtigen Zustand des europäischen Münzwesens. (Platin als Münzmetall.) Pt.  
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- 1878: 42. M. BERTHELOT. Sur les affinités relatives et déplacements  
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- 1878: 43. J. THOMSEN. Thermochemische Untersuchungen. Ueber  
die Constitution der wasserhaltigen Salze. (Chlorplatinates, p.  
38 and ff.) Pt.  
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Jsb. Chem. 1878, 88, 90.
- 1878: 44. J. VIOLLE. Chaleur spécifique et chaleur de fusion du palla-  
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(1879), 192.
- 1878: 45. R. SABINE. Motions produced by dilute acids on some amal-  
gam surfaces. (Platinum amalgam.) Pt.  
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- 1878: 49. J. N. LOCKYER. Researches in spectrum analysis in connection with the spectrum of the sun. (Palladium found in the sun.) Pd.  
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- 1878: 50. D. TOMMASI. Sull' azione della cosi della forza catalitica spiegata secondo la teoria termodinamica. (Action of platinum sponge on gaseous mixtures.) Pt.  
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- 1878: 51. D. TOMMASI. Riduzione del cloruro di argento e del cloruro ferrico. (By platinum.) Pt.  
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- 1878: 52. F. HOPPE-SEYLER. Ueber Gährungsprozesse. (Action of palladium-hydrogen in decay, p. 21.) Pd, Pt.  
Ztsch. physiol. Chem. 2 (1878), 1; Jsb. Chem. 1878, 1025.
- 1878: 53. J. H. GLADSTONE and A. TRIBE. Analogies between the action of the copper-zinc couple and of occluded and nascent hydrogen. (Reducing action of palladium-hydrogen.) Pt, Pd.  
J. Chem. Soc. 33 (1878), 306; Jsb. Chem. 1878, 191.
- 1878: 54. N. BÉKÉTOFF. (Ermittelung der Wärmecapazität des Wasserstoffs in seiner Legirung mit Palladium.) Pd.  
J. Russ. Chem. Soc. 11, i (1878), 4; Ber. 12 (1879), 686; Bul. soc. chim. [2], 31 (1879), 197; Chem. Centrbl. 1879, 242; Jsb. Chem. 1879, 91; J. Chem. Soc. 36 (1879), 590.
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- 1878: 57. W. BEETZ. Ueber die Electricitätserregung beim Contact fester und gasförmiger Körper. (Contact of gases with platinum and palladium.) Pt, Pd.  
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- 1878: 58. F. EXNER. Ueber die galvanische Polarisation des Platins in Wasser. Pt.  
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(Preparation of pure platinum, p. 176; occluded hydrogen on  
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1005.
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Bul. soc. chim. [2], 33 (1880), 250, 402; Ber. 13 (1880), 925; Chem. Centrbl. 1880, 277; J. Amer. Chem. Soc. 2 (1880), 363, 430; Jsb. Chem. 1880, 403.
- 1880: 11. R. SCHOLTZ. Ueber einige Platincyandoppelverbindungen. (With measurements of crystals.) Pt.  
Sitzber. Akad. Wien, 82, ii (1880), 1233; Ber. 14 (1881), 514; Monatsh. f. Chem. 1 (1880), 900; Jsb. Chem. 1881, 320; J. Chem. Soc. 40 (1881), 707; Chem. Ztg. 5 (1881), 60.
- 1880: 12. A. RICHARD and A. BERTRAND. Sur le platinocyanure double de magnésium et de potassium. Pt.  
Bul. soc. chim. [2], 34 (1880), 630; Ber. 14 (1881), 108; Chem. Centrbl. 1881, 38; Jsb. Chem. 1880, 364.
- 1880: 13. P. T. CLEVE. Om erbinjorden. (Erbium chloroplatinate.) Pt.  
Oefversigt. Akad. Förh. Stockholm, 37 (1880), No. 7, 3; C. R. 91 (1880), 381; Jsb. Chem. 1880, 305.
- 1880: 14. W. SPRING. Recherches sur la propriété que possèdent les corps de se souder sous l'action de la pression. (Platinum, Ann. chim. phys., p. 187.) Pt.  
Bull. Acad. Bruxellés, 49 (1880), 323; Rev. Univ. des Mines [2], 8 (1880), 470; Ann. chim. phys. [5], 22 (1881), 170.
- 1880: 15. A. DITTE. Action de l'acide chlorhydrique sur les chlorures métalliques. (On platinum tetrachlorid.) Pt.  
C. R. 91 (1880), 986; Ann. chim. phys. [5], 22 (1881), 551; Chem. Centrbl. 1881, 36; Jsb. Chem. 1881, 154.
- 1880: 16. V. MEYER. Einige Versuche über die Dampfdichten der Alkalimetalle. (Action of potassium and sodium on platinum.) Pt.  
Ber. 13 (1880), 391.

- 1880: 17. J. M. EDER. Ueber die hervorragenden reducirenden Eigenschaften des Kaliumferrooxalates und einige durch dasselbe hervorgerufene Reactionen. (Reduction of chlorid of platinum.) Pt.  
Sitzber. Akad. Wien, 81, ii (1880), 196; Ber. 13 (1880), 500; Chem. Indust. 3 (1880), 142; Jsb. Chem. 1880, 770; Monatsh. f. Chem. 1 (1880), 137; Ztsch. anal. Chem. 21 (1882), 107.
- 1880: 18. T. L. PHIPSON. On the reduction of auric chloride by hydrogen in presence of platinum. (Hydrogen condensed on platinum.) Chem. News, 41 (1880), 13; Jsb. Chem. 1880, 361. Pt.
- 1880: 19. D. TOMMASI. On the reduction of chloride of gold by hydrogen in the presence of platinum. (Hydrogen condensed on platinum.) Pt.  
Chem. News, 41 (1880), 116; Jsb. Chem. 1880, 361.
- 1880: 20. H. GOLDSCHMIDT. Die Valenz des Phosphors. (Note on action of platinum on phosphorus pentachlorid.) Pt.  
Jsb. Lese- u. Redehalle d. deutsch. Stud. Prag, 1880-81; Chem. Centrbl. 1881, 489; Jsb. Chem. 1881, 188.
- 1880: 21. A. CERTES. Sur l'analyse micrographique des eaux. (Osmium tetroxid in water analysis.) Os.  
C. R. 90 (1880), 1435; Jsb. Chem. 1880, 1144.
- 1880: 22. C. VINCENT. Note sur les réactions produites par la diméthylamine aqueuse sur les dissolutions métalliques. (On platinum and palladium solutions.) Pt, Pd.  
Bul. soc. chim. [2], 33 (1880), 156; Chem. Centrbl. 1880, 278; Ztsch. anal. Chem. 19 (1880), 480.
- 1880: 23. T. T. MORRELL. Estimation of small quantities of potash with platinic chloride. Pt.  
J. Amer. Chem. Soc. 2 (1880), 145; Ber. 13 (1880), 1886; Chem. Ztg. 4 (1880), 509; Jsb. Chem. 1880, 1173; Dingl. pol. J. 241 (1881), 140.
- 1880: 24. J. VON FODOR. (Palladium chlorid as reagent for carbon monoxid.) Pd.  
Deutsch. Vierteljsch. off. Gesundhpflege. 12 (1880), 377; Ztsch. anal. Chem. 22 (1883), 81; Jsb. Chem. 1883, 1555.
- 1880: 25. H. VON JÜPTNER. Die Trennung des Goldes mittelst Cadmium. (From the platinum metals.) Pt, Pd, Ir, Rh, Os, Ru.  
Oester. Ztsch. Bergwesens, 28 (1880), 182; Chem. Ztg. 4 (1880), 276; Jsb. Chem. 1880, 1196.

- 1880: 26. C. LUCKOW. Ueber die Anwendung des elektrischen Stromes in der analytischen Chemie. (Electrolytic determination of platinum, p. 13.) Pt.  
Ztsch. anal. Chem. 19 (1880), 1; Chem. News, 41 (1880), 213; Dingl. pol. J. 239 (1881), 307; Jsb. Chem. 1880, 1140.
- 1880: 27. L. SCHUCHT. Zur Elektrolyse. (Electrolytic determination of palladium.) Pt.  
Berg und Hütten Ztg. 39 (1880), 121; Chem. News, 41 (1880), 280; Chem. Centrbl. 1880, 374; Chem. Ztg. 4 (1880), 293; Jsb. Chem. 1880, 174, 1143.
- 1880: 28. J. H. DEBRAY. Action des acides sur les alliages du rhodium avec le plomb et le zinc. (Also lead alloys with the other platinum metals.) Rh, Pt, Pd, Ir, Os, Ru.  
C. R. 90 (1880), 1195; Chem. Centrbl. 1880, 433; Chem. News, 41 (1880), 295; J. Chem. Soc. 38 (1880), 706; Jsb. Chem. 1880, 368; J. Russ. Chem. Soc. 12, ii (1880), 377.
- 1880: 29. A. D. VAN RIEMSDIJK. Le phénomène de l'éclair dans les essais d'or et l'influence exercée sur ce phénomène par les métaux du groupe du platine. Pt, Pd, Ir, Os, Ru.  
Archiv. Néerland. 15 (1880), 185; Ann. chim. phys. [5], 20 (1880), 66; Chem. News, 41 (1880), 126, 266; Ber. 13 (1880), 936; Berg und Hütten Ztg. 39 (1880), 247, 275.
- 1880: 30. E. WIEDEMANN. Ueber das durch elektrische Entladungen erzeugte Phosphoreszenzlicht. (Electrischer Dichroismus des Platincyanbariums.) Pt.  
Ann. der Phys. (Pogg.) [2], 9 (1880), 157; Jsb. Chem. 1880, 186.
- 1880: 31. E. LOMMEL. Ueber die Erscheinungen, welche eine senkrecht zur optischen Axe geschnittene Platte von Magnesiumplatin-cyanür im polarisirten Licht zeigt. Pt.  
Sitzber. Phys. Med. Soc. Erlangen, 12 (1880), 33; Ann. der Phys. (Pogg.) [2], 9 (1880), 108; Repert. Exp. Phys. 17 (1881), 254.
- 1880: 32. E. LOMMEL. Ueber Fluorescenz. (Platinum cyanids.) Pt.  
Sitzber. Phys. Med. Soc. Erlangen, 12 (1880), 53; Ann. der Phys. (Pogg.), 10 (1880), 449, 631; Repert. Exp. Phys. 16 (1880), 733.
- 1880: 33. P. GROTH (L. CALDERON, J. H. VANT'HOFF, A. HOWE, A. FOCK). (Crystallography of the platinum iodonitrites.) Pt.  
Ztsch. Kryst. 4 (1880), 492; Jsb. Chem. 1880, 363.
- 1880: 34. F. BEILSTEIN. (Loss of weight of platinum crucibles by heating.) Pt.  
Pharm. Ztsch. Russ. 19 (1880), 630; J. Russ. Chem. Soc. 12, i (1880), 298; Chem. Centrbl. 1880, 614; Jsb. Chem. 1880, 1145; Ztsch. anal. Chem. 20 (1881), 407.



- 1880: 35. A. SCHEURER-KESTNER. Sur la dissolution du platine dans l'acide sulfurique. (During concentration.) Pt.  
C. R. 91 (1880), 59; Ber. 13 (1880), 1975; Chem. Centrbl. 1880, 564; Chem. News, 42 (1880), 61; J. Chem. Soc. 38 (1880), 706; Jsb. Chem. 1880, 361; J. Russ. Chem. Soc. 13, ii (1881), 46.
- 1880: 36. F. KUHLMANN (FILS). Explosion d'un alambic de platine servant à la concentration de l'acide sulfurique. Pt.  
Bul. soc. chim. [2], 33 (1880), 50, 97; Dingl. pol. J. 237 (1880), 253; J. Chem. Soc. 38 (1880), 517; Jsb. Chem. 1880, 1249; J. Amer. Chem. Soc. 2 (1880), 130; Analyst, 5 (1880), 10; Chem. Ztg. 4 (1880), 8.
- 1880: 37. C. FABRE. (Platinotypie.) Pt.  
Bul. de l'Assoc. Belge. de Phot. 6, 302; Photog. Corresp. 17 (1880), 38; Chem. Centrbl. 1880, 383; Dingl. pol. J. 237 (1880), 416; Jsb. Chem. 1880, 1393; Chem. tech. Mitth. (Elsner), 30 (1880-81), 273.
- 1880: 38. M. BERTHELOT. Sur quelques relations générales entre la masse chimique des élémens et la chaleur de formation de leur combinaisons. (Platinum and palladium compounds.) Pt, Pd.  
Ann. chim. phys. [5], 21 (1880), 386; C. R. 90 (1880), 1511; 91 (1880), 17; Rev. scient. 19 (1880), 26; Jsb. Chem. 1880, 134.
- 1880: 39. P. DESAINS and P. CURIE. Recherches sur la détermination des longueurs d'onde des rayons calorifiques à basse température. (Of glowing platinum.) Pt.  
C. R. 90 (1880), 1506; Jsb. Chem. 1880, 196.
- 1880: 40. E. BOUTY. Mesure des forces électromotrices thermoélectriques au contact d'un métal et d'un liquide. (Platinum and liquids.) Pt.  
C. R. 90 (1880), 917; Séanc. Soc. Phys. Paris, 1880, 96; Jsb. Chem. 1880, 160.
- 1880: 41. G. GORE. On the thermo-electric behaviour of aqueous solutions with platinum electrodes. Pt.  
Proc. Roy. Soc. London, 31 (1881), 244.
- 1880: 42. C. A. YOUNG. On the thermo-electric power of iron and platinum in vacuo. Pt.  
Amer. J. Sci. [3], 20 (1880), 358; Phil. Mag. [5], 10 (1880), 450.
- 1880: 43. R. BLONDLOT. Sur une nouvelle propriété électrique du sélénium et sur l'existence des courants tribo-électriques proprement dits. (Selenium and platinum in contact.) Pt.  
C. R. 91 (1880), 882; Séanc. Soc. Phys. Paris, 1880, 196; Repert. Exp. Phys. 17 (1881), 259; Jsb. Chem. 1880, 175.

- 1880: 44. E. H. HALL. On a new action of magnetism on a permanent electric current. (Platinum, *Phil. Mag.*, p. 321.) Pt.  
*Amer. J. Sci.* [3], 20 (1880), 161; *Phil. Mag.* [5], 10 (1880), 301; *Jsb. Chem.* 1880, 172, 173.
- 1880: 45. H. HELMHOLTZ. Ueber Bewegungsströme am polarisirten Platina. Pt.  
*Monatsber. Akad. Berlin*, 1880, 285; *Ann. der Phys. (Pogg.)* [2], 11 (1880), 737.
- 1881: 1. W. E. HIDDEN. Notes on mineral localities in North Carolina. (No platinum in five localities.) Pt.  
*Amer. J. Sci.* [3], 22 (1881), 25; *Jsb. Chem.* 1881, 1347.
- 1881: 2. P. COLLIER. A remarkable nugget of platinum. (From Plattsburgh, N. Y.; with analysis.) Pt, Pd, Ir, Os, Rh, Ru.  
*Amer. J. Sci.* [3], 21 (1881), 123; *Ztsch. Kryst.* 5 (1881), 515; *Jsb. Chem.* 1881, 1347; *J. Chem. Soc.* 44 (1883), 426; *Jahrb. f. Min.* 1883, 1, Ref. 27.
- 1881: 3. ———. Gold and platinum in Russia. Pt.  
*Engineering*, 31 (1881), 163; *Dingl. pol. J.* 240 (1881), 152; *J. Chem. Soc.* 40 (1881), 769.
- 1881: 4. ———. Increased importance of iridium. Ir.  
*Scient. Amer.* 44 (1881), 369; *Berg und Hütten Ztg.* 40 (1881), 327; *Chem. Centrbl.* 1882, 47.
- 1881: 5. T. WILM. (Beiträge zur Chemie der Platinmetalle.) (Purification of palladium; precipitation of rhodium and palladium; solution of platinum metals in hydrochloric acid; rhodium and hydrogen.) Rh, Pd, Pt, Ir, Os, Ru.  
*J. Russ. Chem. Soc.* 13, i (1881), 360, 517, 560; *Ber.* 14 (1881), 629; 15 (1882), 241 (abst.); *Bul. soc. chim.* [2], 36 (1881), 436; 37 (1882), 344, 545; 38 (1882), 139, 167; *Chem. Centrbl.* 1881, 321; 1882, 23, 153; *Dingl. pol. J.* 240 (1881), 325; 244 (1882), 87; *J. Chem. Soc.* 40 (1881), 514; *Jsb. Chem.* 1881, 306; 1882, 359, 1389; *Chem. Ztg.* 5 (1881), 252; *Chem. tech. Mitth. (Elsner)*, 30 (1880-81), 219.
- 1881: 6. T. WILM. (Ueber das Verhalten von Palladium, Rhodium und Platin zu Leuchtgas.) Pd, Rh, Pt.  
*J. Russ. Chem. Soc.* 13, i (1881), 490; *Ber.* 14 (1881), 874; *Amer. Chem. J.* 3 (1881), 154; *Bul. soc. chim.* [2], 36 (1881), 438; *Dingl. pol. J.* 241 (1881), 150; *J. Chem. Soc.* 40 (1881), 706; *Jsb. Chem.* 1881, 307; *Chem. Ztg.* 5 (1881), 323.
- 1881: 7. W. GIBBS. On osmyl-ditetramin. Os.  
*Amer. Chem. J.* 3 (1881), 233; *Ber.* 14 (1881), 2820; *J. Chem. Soc.* 42 (1882), 144; *Jsb. Chem.* 1881, 308; *J. Russ. Chem. Soc.* 14, ii (1882), 207.

- 1881: 8. O. HESSE. Neue Platinsalze. (Chlorplatinates of quinin derivatives.) Pt.  
Ann. der Chem. (Liebig), 207 (1881), 309; Chem. News, 44 (1881), 83; J. Chem. Soc. 40 (1881), 922; Monit. scient. 23 (1881), 1122; Chem. Ztg. 5 (1881), 400.
- 1881: 9. K. SEUBERT. Ueber das Atomgewicht des Platins (194.177). Pt.  
Ann. der Chem. (Liebig), 207 (1881), 1; Ber. 14 (1881), 865; Pharm. Ztsch. Russ. 20 (1881), 256; Amer. Chem. J. 3 (1881), 157; Amer. J. Sci. [3], 21 (1881), 398; Bul. soc. chim. [2], 36 (1881), 437; Chem. Centrbl. 1881, 321; Chem. News, 43 (1881), 252; 44 (1881), 82; J. Chem. Soc. 40 (1881), 514; Jsb. Chem. 1881, 6; J. Russ. Chem. Soc. 14, ii (1882), 64; Chem. Ztg. 5 (1881), 217; Repert. anal. Chem. 1 (1881), 151.
- 1881: 10. A. ORLOWSKY. (Affinity between platinum and sulfur.) Pt.  
J. Russ. Chem. Soc. 13, i (1881), 547; Ber. 14 (1881), 2823; Jsb. Chem. 1881, 24.
- 1881: 11. E. POMEY. Sur les combinaisons phosphoplatiniques. Pt.  
C. R. 92 (1881), 794; Bul. soc. chim. [2], 35 (1881), 420; Chem. Centrbl. 1881, 322; Chem. News, 43 (1881), 222; Jsb. Chem. 1881, 305.
- 1881: 12. P. SCHÜTZENBERGER. Carbone de platine. Pt.  
Bul. soc. chim. [2], 35 (1881), 355; J. Russ. Chem. Soc. 14, ii (1882), 149.
- 1881: 13. F. W. CLARKE and MARY E. OWENS. Some new compounds of platinum. (Action of potassium cyanate on platinum tetrachlorid and on Magnus' salt; potassium thiocyanate on platinum tetrachlorid; and hydrogen sulfid on strychnin chloroplatinate.) Pt.  
Amer. Chem. J. 3 (1881), 351; Ber. 15 (1882), 352; Chem. News, 45 (1882), 62; Bul. soc. chim. [2], 37 (1882), 400; Chem. Centrbl. 1882, 153; J. Chem. Soc. 42 (1882), 299; Jsb. Chem. 1881, 305; Scient. Proc. Ohio Mech. Inst. 1 (1882), 45; Chem. Ztg. 6 (1882), 69.
- 1881: 14. S. M. JÖRGENSEN. Beiträge zur Chemie der Kobaltammoniakverbindungen. (Chlorplatinates.) Pt.  
J. prakt. Chem. [2], 23 (1881), 227; Bul. soc. chim. [2], 36 (1881), 311; Jsb. Chem. 1881, 251.
- 1881: 14A. A. COLSON. Sur la diffusion des solides dans les solides. (Platinum does not react with carbon.) Pt.  
C. R. 93 (1881), 1074; Jsb. Chem. 1881, 79.

- 1881: 15. J. HOLLAND. Process of fusing and moulding iridium. (By fusion with phosphorus.) (U. S. Patent, 241216; D. R. pat., 15979, May 10, 1881.) Ir.  
J. Amer. Chem. Soc. 3 (1881), 158; Dingl. pol. J. 244 (1882), 219; Oester. Ztsch. Berg und Hütten Wesen, 29 (1881), 678; Chem. Centrbl. 1882, 334; Jsb. Chem. 1882, 1388; Chem. tech. Mitth. (Elsner), 31 (1881-82), 105.
- 1881: 16. F. W. CLARKE. An abstract of the results obtained in a recalculation of the atomic weights. (Platinum metals, Phil. Mag., p. 108; Am. C. J., p. 271.) Pt, Pd, Ir, Rh, Os, Ru.  
Phil. Mag. [5], 12 (1881), 101; Amer. Chem. J. 3 (1881), 263; Jsb. Chem. 1881, 7.
- 1881: 17. J. DEWAR and A. SCOTT. On some vapor density determinations. (Platinum bichlorid.) Pt.  
Rept. Brit. Assoc. 1881, 597; Ann. der Phys. (Pogg.), Beibl. 7 (1883), 149; Jsb. Chem. 1883, 48.
- 1881: 18. G. CAMPARI. Ricerca dell' oro e platino in presenza dell' arsenico, dello stagno e dell' antimonio. (Quantitative separation of platinum from arsenic, tin and antimony.) Pt.  
Annali di chim. 74 (1882), 1; Ber. 15 (1882), 958; Chem. Ztg. 6 (1882), 161.
- 1881: 19. F. FIELD. Laboratory observations: On the detection of small quantities of platinum; action of organic substances in reaction with platinum iodide and potassium iodide in water analysis. Pt (Pd, Rh).  
Chem. News, 43 (1881), 75, 180; Ber. 14 (1881), 693, 1296; Chem. Centrbl. 1881, 251; J. Chem. Soc. 40 (1881), 649; Ztsch. anal. Chem. 21 (1882), 421; 22 (1883), 252; Jsb. Chem. 1882, 1260; J. Russ. Chem. Soc. 13, ii (1881), 340.
- 1881: 20. D. LINDO. Estimation of potassium as platinum salt. Pt.  
Chem. News, 44 (1881), 77, 86, 97, 129; Ztsch. anal. Chem. 21 (1882), 406.
- 1881: 21. G. ULEX. Ueber Kalibestimmung als Kaliumplatinchlorid. Pt.  
Rept. anal. Chem. 1 (1881), 306; Ztsch. anal. Chem. 22 (1883), 560.
- 1881: 22. R. R. TATLOCK. On the determination of potassium as potassium platino-chloride. Pt.  
Chem. News, 43 (1881), 273.
- 1881: 23. S. ZUCKSCHWERDT and B. WEST. Ueber die Bestimmung des Kaliums als Kaliumplatinchlorid. Pt.  
Ztsch. anal. Chem. 20 (1881), 185; Dingl. pol. J. 241 (1881), 140; Chem. News, 43 (1881), 251.

- 1881: 24. O. WALLACH. Zur Analyse von organischen Platinsalzen.  
(Note.) Pt.  
Ber. 14 (1881), 753; Bul. soc. chim. [2], 36 (1881), 575; Chem.  
Centrbl. 1881, 389; J. Chem. Soc. 40 (1881), 715; Jsb. Chem. 1881,  
1194; Chem. News, 47 (1883), 249; Chem. Ztg. 5 (1881), 289.
- 1881: 25. L. MAGGI. Sull' analisa protistologica delle acque potabili.  
(Use of palladium chlorid in place of osmium tetroxid in water  
analysis.) Pd, Os.  
Le stazioni sperimentali agrarie ital. 11 (1882), 28; Rendic. Inst.  
Lomb. Milano, 14 (1881), 621; Gazz. chim. ital. 13 (1883), 323;  
Rev. scient. 3 (1882), 661; Jsb. Chem. 1883, 1526.
- 1881: 26. A. TSCHIRIKOFF (SCHIRIKOW). (Use of palladium in esti-  
mation of hydrogen.) Pd.  
J. Russ. Chem. Soc. 14, i (1882), 47; Bul. soc. chim. [2], 38 (1882),  
171; Chem. Centrbl. 1882, 821; Jsb. Chem. 1882, 59, 1263; Ztsch.  
anal. Chem. 22 (1883), 240; Ber. 15 (1882), 958; Ann. der Phys.  
(Pogg.) Beibl. 8 (1884), 629; Chem. Ztg. 8 (1884), 1289; Repert.  
anal. Chem. 2 (1882), 120.
- 1881: 27. [R.?] SCHNEIDER. Ueber das Palladiumchlorür als Reagens  
auf Kohlenoxyd. Pd.  
Repert. anal. Chem. 1 (1881), 54; Chem. Centrbl. 1881, 201.
- 1881: 28. A. RÉMONT. De l'attaque du platine sous l'influence de la  
flamme. (Crucibles.) Pt.  
Bul. soc. chim. [2], 35 (1881), 353 (note), 486; Ber. 14 (1881), 1394;  
Chem. Centrbl. 1881, 440; Chem. News, 44 (1881), 169; J. Chem.  
Soc. 40 (1881), 882; Jsb. Chem. 1881, 304; School of Mines (N. Y.)  
Quart. 3 (1882), 301; J. Russ. Chem. Soc. 14, ii (1882), 236;  
Repert. anal. Chem. 1 (1881), 189.
- 1881: 29. C. A. M. BALLING. Beitrag zur Volumetrie einiger Metalle.  
(Influence of platinum in quartation of gold by cadmium.) Pt.  
Oester. Ztsch. Berg- und Hütten-Wesen, 29 (1881), 51; Chem. Ztg.  
5 (1881), 113; Jsb. Chem. 1881, 1156.
- 1881: 30. E. LOMMEL. Ein Polarisationsapparat aus Magnesiumplatin-  
cyanür. Pt.  
Sitzber. Phys. Med. Soc. Erlangen, 13 (1881), 31; Ann. der Phys.  
Pogg. [2], 13 (1881), 347.
- 1881: 31. H. BUSH. Metallurgie des Platins. (Use of platinum al-  
loys.) Pt.  
Centralztg. Optik. Mech. 2 (1881), 30; Dingl. pol. J. 240 (1881),  
216; Polyt. Notizbl. 36 (1881), 54; Repert. anal. Chem. 1 (1881),  
94.

- 1881: 32. ————. Zur Herstellung und Verwendung des Platins. (Editorial review.) Pt.  
Dingl. pol. J. 240 (1881), 213; J. Chem. Soc. 40 (1881), 792.
- 1881: 33. P. CASAMAJOR. (New filtering apparatus.) Pt.  
J. Amer. Chem. Soc. 3 (1881), 123; Chem. News, 45 (1882), 148;  
Monit. scient. 24 (1882), 884.
- 1881: 34. O. J. BROCH, E. H. SAINTE-CLAIRE DEVILLE, and J. S. STAS.  
De la règle en forme d'X et en platine iridié pur à 10 pour 100  
d'iridium. Pt, Ir, Pd, Rh, Os, Ru.  
Ann. chim. phys. [5], 22 (1881), 120; J. Chem. Soc. 40 (1881), 680.
- 1881: 35. ————. (Platindruck.) Pt.  
Photog. Archiv, 27 (1881), 2; Chem. Centrbl. 1881, 175; Dingl. pol.  
J. 240 (1881), 405; J. Chem. Soc. 42 (1882), 115; Jsb. Chem. 1881,  
1342.
- 1881: 36. E. BAUMANN. Zur Kenntniss des aktiven Sauerstoffs. (Pal-  
ladiumwasserstoff.) Pd.  
Ztsch. physiol. Chem. 5 (1881), 244.
- 1881: 37. J. VIOLE. Sur la loi de rayonnement. (Intensités lumi-  
neuses des radiations émises par le platine incandescent.) Pt.  
C. R. 92 (1881), 866, 1204; J. Chem. Soc. 40 (1881), 669; Jsb. Chem.  
1881, 116; Phil. Mag. [5], 13 (1882), 147.
- 1881: 38. E. L. NICHOLS. Note on the electrical resistance and the  
coefficient of expansion of incandescent platinum. Pt.  
Proc. Amer. Assoc. 1881, 24; Amer. J. Sci. [3], 22 (1881), 363;  
Phil. Mag. [5], 13 (1882), 38; Ber. 15 (1882), 524; J. Chem. Soc. 42  
(1882), 354; Jsb. Chem. 1881, 94; 1882, 149.
- 1881: 39. F. STREINTZ. Ueber die durch Entladung von Leydener  
Flaschen hervorgerufene Zersetzung des Wassers an Platinelektro-  
den. Pt.  
Sitzber. Akad. Wien, 83, ii (1881), 618; Anzeiger Akad. Wien, 18  
(1881), 67; Ann. der Phys. (Pogg.), [2], 13 (1881), 644.
- 1881: 40. G. H. JOHNSON. On the synthetical production of ammonia  
by the combination of hydrogen and nitrogen in presence of  
heated spongy platinum. Pt.  
J. Chem. Soc. 39 (1881), 128, 130; J. Russ. Chem. Soc. 14, ii (1882),  
146.
- 1882: 1. A. VON LASAULX. Ueber einen ausgezeichneten Krystall von  
dunklem Osmiridium aus dem Ural. (Crystallographic.) Os, Ir.  
Sitzber. Niederrhein. Gesell. Bonn, 39 (1882), 99; Ztsch. Kryst. 8  
(1884), 303; Jsb. Chem. 1884, 1902.

- 1882: 2. W. H. SEAMON. Examination of gold, silver, etc., alloys found in grains along with the native platinum of Colombia, S. America. Pt.  
Chem. News, 46 (1882), 215; J. Chem. Soc. 44 (1883), 160; Jsb. Chem. 1882, 1522.
- 1882: 3. W. H. SEAMON. Analysis of native palladium-gold from Taguaril, near Subara, province of Minas Geraes, Brazil. Pd.  
Chem. News, 46 (1882), 216; J. Chem. Soc. 44 (1883), 160; Chem. Centrbl. 1882, 819; Jsb. Chem. 1882, 1522.
- 1882: 4. J. W. MALLET. Comment on W. H. Seamon's analysis of palladium-gold from Brazil. Pd.  
Chem. News, 46 (1882), 216; Jsb. Chem. 1882, 1522.
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Sci. [3], 37 (1889), 75; Chem. Centrbl. 1888, 964; Chem. News,  
59 (1889), 179; J. Chem. Soc. 54 (1888), 921; Ztsch. anal. Chem.  
28 (1889), 139; Ztsch. angew. Chem. (1888), 422; Jsb. Chem.  
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- 1889: 20. C. WINKLER. Beiträge zur technischen Gasanalyse. (Use of palladium chlorid for detection of carbon monoxid.) Pd.  
Ztsch. anal. Chem. 28 (1889), 269; J. Soc. Chem. 56 (1889), 924.
- 1889: 21. K. JAHN. Ueber synthetische Bildung von Formaldehyde. (By action of palladium-hydrogen on carbon monoxid.) Pd,  
Ber. 22 (1889), 989; Jsb. Chem. 1889, 1468.
- 1889: 22. H. VON JÜPTNER. (Veraschen in Platintiegel.) Pt.  
Chem. Ztg. 13 (1889), 1303; Chem. Centrbl. 1889, ii, 1011.
- 1889: 23. ————. (Glas zu platiniren.) Pt.  
Sprechsaal, 22 (1889), No. 3; Dingl. pol. J. 271 (1889), 528; Jsb. Chem. 1889, 2691.
- 1889: 24. M. TRAUBE. Zur Lehre von der Autoxydation. (Action of palladium hydrogen.) Pd, Pt.  
Ber. 22 (1889), 1496, 3057; J. Chem. Soc. 56 (1889), 937; Jsb. Chem. 1889, 384.
- 1889: 25. F. HOPPE-SEYLER. Ueber die Activirung des Sauerstoffs durch Wasserstoff. (Reply to M. Traube.) Pd.  
Ber. 22 (1889), 2215.
- 1889: 26. M. THOMA. Ueber die Absorption von Wasserstoff durch Metalle. Pd.  
Ztsch. physik. Chem. 3 (1889), 69; Ber. 22 (1889), 184; J. Chem. Soc. 56 (1889), 568; Chem. News, 60 (1889), 25; Phil. Mag. [5], 28 (1889), 351; Ann. der Phys. (Pogg.) Beibl. 13 (1889), 529; Jsb. Chem. 1889, 342.

- 1889: 27. L. ILOSVAY DE N. ILOVA. Union d'azote et oxygène par le platine. Pt.  
Soc. hongroise sci. nat. Oct. 12, 1889; Bul. soc. chim. [3], 2 (1889), 738; J. Chem. Soc. 58 (1890), 447.
- 1889: 28. ———. (Platinuranotypie.) Pt.  
Brit. J. Phot.; Phot. Mittheilung, 25 (1889), 303; Chem. Ztg. 13 (1889), Rep. 68.
- 1889: 29. K. FUCHS. (Ueber Liebreich's toten Raum und das Glühen des Platins in Alkoholdampf.) Pt.  
Chem. Centrbl. 1889, ii, 176; from Repert. d. Physik.
- 1889: 30. F. VON BRÜHL. (Platinum in photography.) Pt.  
Phot. Archiv, 1889, 154; Dingl. pol. J. 274 (1889), 34.
- 1889: 31. J. SCHNAUSS. Pizzighelli's neues Platinpapier. (For photography.) Pt.  
Chem. Ztg. 13 (1889), 390.
- 1889: 32. ———. (Kalte Platinentwicklung.) Pt.  
Brit. J. Phot.; Phot. Wochenbl. 15 (1889), 25; Chem. Ztg. 13 (1889), Rep. 52.
- 1889: 33. J. M. EDER. Ueber die Fortschritte der Photographie und der photomechanischen Druckverfahren. Pt.  
Dingl. pol. J. 274 (1889), 34; Jsb. Chem. 1889, 2876.
- 1889: 34. ———. Neues Platinonverfahren. Pt.  
Bul. soc. phot. Franç.; Phot. Nachr. 1 (1889), 166; Chem. Ztg. 13 (1889), Rep. 360.
- 1889: 35. C. R. CRAWFORD. An improved method of deciding the correct exposure of platinotype printing and an apparatus therefor. Engl. patent 10504, June 28, 1889. Pt.  
J. Soc. Chem. Ind. 9 (1890), 651.
- 1889: 36. P. MERCIER. Sur une méthode générale de virage des épreuves photographiques aux sels d'argent, au platine et aux métaux du groupe du platine. Pt, Ir, Os.  
C. R. 109 (1889), 949; J. Frank. Inst. [3], 99 (1890), 149; Jsb. Chem. 1889, 2882; Bul. soc. franç. photog. 1890, 195; Dingl. pol. J. 283 (1892), 19.
- 1889: 37. A. WILLIS. (Platinum in photography.) Pt.  
Phot. Nachr. 1889, 35; Phot. Rundsch. Steiglitz, 1889, 111; Dingl. pol. J. 274 (1889), 34; 283 (1892), 18.
- 1889: 38. R. EMDEN. Ueber den Beginn der Lichtermission glühender Metalle. (Palladium and platinum.) Pd, Pt.  
Ann. der Phys. (Pogg.) [2], 36 (1889), 214; Jsb. Chem. 1889, 310.

- 1889: 39. F. RICHARZ. Ueber das elektromotorische Verhalten von Platin in Ueberschwefelsäure und über die galvanische Polarisation bei der Bildung derselben. Pt.  
Ztsch. physik. Chem. 4 (1889), 18; Chem. Centrbl. 1889, ii, 433; Jsb. Chem. 1889, 298.
- 1889: 40. PRATT. (Soldering platinum crucibles.) Pt.  
Revue scientif.; J. pharm. chim. [5], 20 (1889), 276; Pharm. Post (Wien), 22 (1889), 814; Chem. Centrbl. 1890, i, 10.
- 1889: 41. H. LE CHATELIER. Sur la dilation des métaux aus températures élevées. (Expansion of platinum and platinum-iridium.) C. R. 108 (1889), 1096; Jsb. Chem. 1889, 151. Pt, Ir.
- 1889: 42. PIZZIGHELLI. Der Platindruck. Pt.  
Phot. Arch. 29, 301; Dingl. pol. J. 274 (1889), 34; Chem. Centrbl. 1889, i, 87; Jsb. Chem. 1889, 2876, 2882.
- 1890: 1. C. BLÖMEKE. Ueber das Vorkommen und die Production von Zinn, Nickel, Platin und Quecksilber auf der Erde. (Platinum ore.) Pt.  
Berg und Hütten Ztg. 49 (1890), 237.
- 1890: 2. LAURENT. L'industrie de l'or et du platine dans l'Oural. Pt.  
Ann. des Mines [8], 18 (1890), 537; Berg und Hütten Ztg. 50 (1891), 435; J. Soc. Chem. Ind. 11 (1892), 532; Eng. and Min. J. 53 (1892), 430.
- 1890: 3. F. W. CLARKE and C. CATLETT. A platiniferous nickel ore from Canada. Pt.  
Bul. U. S. Geol. Survey, No. 64 (1890), 20; Chem. News, 67 (1893), 53; Chem. Ztg. 17 (1893), Rep. 44; J. Chem. Soc. 64, ii (1893), 286.
- 1890: 4. ————. Platinausbeute in Russland 1888-90. Pt, Pd, Ir, Os.  
Chem. Indust. 13 (1890), 432; J. Soc. Chem. Ind. 9 (1890), 1077.
- 1890: 5. G. TROTTARELLI. Analisi chimica dell' aereolite caduto a Collescipoli presso Terni il 3 Febbraio 1890. (Palladium in a meteorite.) Pd.  
Gazz. chim. ital. 20 (1890), 611; J. Chem. Soc. 60 (1891), 533.
- 1890: 6. ————. Production of platinum. Pt.  
Board of Trade J. 1890, 558; J. Soc. Chem. Ind. 9 (1890), 1040.
- 1890: 7. ————. Robbery of platinum at Messrs. Dunn & Co., Stirling Chemical Works. Pt.  
Chem. News, 62 (1890), 214.

- 1890: 8. M. VÈZES. Sur un chloroplatinate nitrosé. (Platinum nitrosochlorid.) Pt.  
C. R. 110 (1890), 757; Ber. 23 R. (1890), 377; Bul. soc. chim. [3], 4 (1890), 848; Chem. Centrbl. 1890, i, 932; J. Chem. Soc. 58 (1890), 709.
- 1890: 9. K. SEUBERT and K. KOBBE. Ueber das Atomgewicht des Rhodiums (102.7, O = 15.96). Rh.  
Ann. Chem. (Liebig), 260 (1890), 314; Ber. 24 (1891), R. 107; Bul. soc. chim. [3], 5 (1891), 954; J. Chem. Soc. 60 (1891), 646; Chem. Ztg. 15 (1891), Rep. 21; Ztsch. anal. Chem. 31 (1892), 237.
- 1890: 10. K. SEUBERT and K. KOBBE. Ueber die Zusammensetzung einiger Doppelsalze des Rhodiums. (Double chlorids, sulfates, and sulfites, and platinum and iridium sulfites.) Rh, Pt, Ir.  
Ber. 23 (1890), 2556; Bul. soc. chim. [3], 4 (1890), 833; Chem. Centrbl. 1890, ii, 736; J. Chem. Soc. 58 (1890), 1383.
- 1890: 11. G. GEISENHEIMER. Sur la préparation du binoxyde d'iridium. Ir.  
C. R. 110 (1890), 855; Ber. 23 (1890), R. 379; Bul. soc. chim. [3], 4 (1890), 390; Chem. Centrbl. 1890, i, 960; Chem. News, 61 (1890), 228; J. Chem. Soc. 58 (1890), 948; Chem. Ztg. 14 (1890), Rep. 148.
- 1890: 12. G. GEISENHEIMER. Sur les chlorures doubles d'iridium et de phosphore. Ir.  
C. R. 110 (1890), 1004; Ber. 23 (1890), R. 380; Bul. soc. chim. [3], 4 (1890), 391; Chem. Centrbl. 1890, i, 1019; Chem. News, 61 (1890), 265; J. Chem. Soc. 58 (1890), 1068.
- 1890: 13. G. GEISENHEIMER. Combinaisons des chlorures doubles de phosphore et d'iridium avec le chlorure d'arsenic. Ir.  
C. R. 110 (1890), 1336; Ber. 23 (1890), R. 550; Bul. soc. chim. [3], 6 (1891), 1006; Chem. Centrbl. 1890, ii, 204; J. Chem. Soc. 58 (1890), 1069.
- 1890: 14. G. GEISENHEIMER. Sur les bromures doubles de phosphore et d'iridium. Ir.  
C. R. 111 (1890), 40; Ber. 23 (1890), R. 552; Bul. soc. chim. [3], 6 (1891), 1006; Chem. Centrbl. 1890, ii, 331; J. Chem. Soc. 58 (1890), 1383; Ann. chim. phys. [6], 23 (1891), 231; J. Russ. Chem. Soc. 24, ii (1892), 32.
- 1890: 15. P. SCHÜTZENBERGER. Sur un sulfocarbure de platine. Pt.  
C. R. 111 (1890), 391; Ber. 23 (1890), R. 680; Bul. soc. chim. [3], 5 (1891), 672; Chem. Centrbl. 1890, ii, 688; Chem. News, 62 (1890), 178; J. Chem. Soc. 60 (1891), 19; Chem. Ztg. 14 (1890), Rep. 256.

- 1890: 16. H. LÖNDAHL. Bidrag till kännedomen om platinasulfidbasernas konstitution. Pt.  
Års-skrift. Univ. Lund. 27, ii (1890-91), 3.
- 1890: 17. E. LEIDIE. Recherches sur les nitrites doubles du rhodium. Rh.  
C. R. 111 (1890), 106; Bul. soc. chim. [3], 4 (1890), 809; Ber. 23 (1890), R. 630; Chem. Centrbl. 1890, ii, 332; Chem. News, 62 (1890), 62; 63 (1891), 142; J. Chem. Soc. 58 (1890), 1382; 60 (1891), 808.
- 1890: 18. T. WILM. (Nitrites of rhodium.) Rh.  
J. Russ. Chem. Soc. 22, i (1890), 361; Chem. Ztg. 14 (1890), 1036.
- 1890: 19. A. JOLY. Sur une nouvelle série de combinaisons ammoniacales du ruthénium, dérivées du chlorure nitrosé. Ru.  
C. R. 111 (1890), 969; Ber. 24 (1891), R. 68; Bul. soc. chim. [3], 5 (1891), 673; Chem. Centrbl. 1891, i, 255; J. Chem. Soc. 60 (1891), 401.
- 1890: 20. A. JOLY. Sur les chlorosels de l'iridium et sur le poids atomique de cet élément (192.75,  $H = 1$ ). Ir.  
C. R. 110 (1890), 1131; Ber. 23 (1890), R. 548; Chem. Centrbl. 1890, ii, 85; Chem. News, 61 (1890), 301; J. Chem. Soc. 58 (1890), 1067; Ztsch. anal. Chem. 89 (1890), 747; Ztsch. physik. Chem. 6 (1890), 375.
- 1890: 21. S. M. JÖRGENSEN. Zur Constitution der Cobaltbasen. I. (Reference to platinum bases.) Pt.  
J. prakt. Chem. [2], 41 (1890), 429.
- 1890: 22. S. M. JÖRGENSEN. Ueber Metaldiaminverbindungen. (Chloroplatinates.) Pt.  
J. prakt. Chem. [2], 41 (1890), 440.
- 1890: 23. S. M. JÖRGENSEN. Zur Constitution der Kobalt-, Chrom- und Rhodiumbasen. II. (Reference also to platinum bases, and chloroplatinates.) Rh, Pt.  
J. prakt. Chem. [2], 42 (1890), 206; Ber. 23 (1890), R. 682; Bul. soc. chim. [3], 6 (1891), 1005; Chem. Centrbl. 1890, ii, 543; J. Chem. Soc. 58 (1890), 1213.
- 1890: 24. A. COSSA. Sopra un nuovo isomero del sale verde del Magnus. (Platosemiaminchlorid.) Pt.  
Gazz. chim. ital. 20 (1890), 725; Ber. 23 (1890), 2503; 24 (1891), R. 388; Chem. Centrbl. 1890, ii, 645; J. Chem. Soc. 58 (1890), 1218; Mém. Accad. Torino [2], 41 (1891), 1; Atti Accad. Lincei Roma [4], 7, i (1891), 3.

- 1890: 25. O. CARLGREN. Om några ammoniakaliska platinaföreningar.  
(Sulfites of platinum base.) Pt.  
Oefversigt Akad. Förh. Stockholm, 47 (1890), 305; Chem. Ztg. 14  
(1890), 1460.
- 1890: 26. O. CARLGREN and P. T. CLEVE. Ueber einige ammoniakalische Platinverbindungen. Pt.  
Oefvers. Akad. Förh. Stockholm, 47 (1890), 305; Ztsch. anorg.  
Chem. 1 (1892), 65; Ber. 25 R. (1892), 544; Chem. Centrbl. 1892,  
i, 555; J. Chem. Soc. 64, ii (1893), 127.
- 1890: 27. L. PIGEON. Chaleur de formation du chlorure platinique.  
Pt.  
C. R. 110 (1890), 77; Chem. Centrbl. 1890, i, 517; J. Chem. Soc. 58  
(1890), 439; Ztsch. physik. Chem. 5 (1890), 274.
- 1890: 28. C. T. HEYCOCK and F. H. NEVILLE. Molecular weights of  
metals when in solution. (Platinum in tin.) Pd.  
J. Chem. Soc. 57 (1890), 376; Proc. Chem. Soc. 1890, 158; Ber. 24  
(1891), R. 693; Ztsch. physik. Chem. 6 (1890), 190.
- 1890: 29. J. UHL. Ueber Einwirkung von Schwefeldioxyd auf Metalle.  
(Palladium and platinum.) Pd, Pt.  
Ber. 23 (1890), 2151; J. Chem. Soc. 58 (1890), 1371.
- 1890: 30. A. CLASSEN. Bestimmung des Atomgewichtes des Wis-  
muths. (Note on presence of iron in platinum, p. 951.) Pt.  
Ber. 23 (1890), 938.
- 1890: 31. R. ENGEL. Sur l'oxydation de l'acide hypophosphoreux par  
un palladium hydrogène en l'absence d'oxygène. Pd.  
C. R. 110 (1890), 786; Ber. 23 (1890), R. 378; J. Chem. Soc. 58 (1890),  
690.
- 1890: 32. O. LOEW. Darstellung eines sehr wirksamen Platinmohrs.  
Pt.  
Ber. 23 (1890), 289; Bul. soc. chim. [3], 4 (1890), 351; Chem.  
Centrbl. 1890, i, 577; Dingl. pol. J. 277 (1890), 383; J. Chem. Soc.  
58 (1890), 453; Chem. Ztg. 14 (1890), Rep. 56; Chem. News, 67  
(1893), 242; Ztsch. anal. Chem. 31 (1892), 690; J. Soc. Chem. Ind.  
9 (1890), 550.
- 1890: 33. O. LOEW. Bildung von Salpetrigsäure und Ammoniak aus  
freiem Stickstoff. (Under the influence of platinum black.) Pt.  
Ber. 23 (1890), 1443; J. Chem. Soc. 58 (1890), 1051.
- 1890: 34. O. LOEW. Katalytische Reduction der Sulfogruppe. (By  
platinum black.) Pt.  
Ber. 23 (1890), 3125; J. Chem. Soc. 60 (1891), 237.



- 1890: 35. H. DUFET. (Crystallography of potassium ruthenate and perruthenate.) Ru.  
Bul. soc. franç. min. 11, 215; Chem. Centrbl. 1890, i, 374.
- 1890: 36. H. DUFET. (Crystallography of nitrosoruthenium derivatives and rhodium oxalates.) Ru, Rh.  
Bul. soc. franç. min. 12, 466; Chem. Centrbl. 1890, i, 247.
- 1890: 37. H. DUFET. (Crystallography of double iridium chlorids.) Ir.  
Bul. soc. franç. min. ; Chem. Centrbl. 1890, ii, 542.
- 1890: 38. J. THIELE. Zum Nachweis des Arsens. Inaug. Diss. Halle A. S., 1890. (3. Ueber die Anwendung des platinirten Zinks im Marsch'schen Apparat.) Pt.  
Ann. Chem. (Liebig), 265 (1891), 63.
- 1890: 39. E. F. SMITH and H. F. KELLER. The action of hydrogen sulphide gas upon metallic amines. (On palladium bases.) Pd.  
Chem. News, 62 (1890), 290; Ber. 23 (1890), 3373; 24 (1891), R. 109; Chem. Centrbl. 1891, i, 135; J. Chem. Soc. 60 (1891), 272.
- 1890: 40. E. F. SMITH and H. F. KELLER. The electrolytic method as applied to palladium. Pd.  
Amer. Chem. J. 12 (1890), 212; J. Frank. Inst. 130 (1890), 233; Ber. 23 (1890), R. 414; Chem. Centrbl. 1890, i, 946; 1891, ii, 85; Chem. News, 63 (1891), 253; J. Chem. Soc. 58 (1890), 831; Ztsch. angew. Chem. 1891, 650; School of Mines (N. Y.) Quart. 11 (1890), 374.
- 1890: 41. E. F. SMITH and L. K. FRANKEL. Electrolytic separations. (Mercury from palladium.) Pd.  
Amer. Chem. J. 12 (1890), 428; Chem. Centrbl. 1890, ii, 267; J. Chem. Soc. 58 (1890), 1029; J. Soc. Chem. Ind. 9 (1890), 1067.
- 1890: 42. E. MATTHEY. The liquation of gold and platinum alloys. Pt.  
Phil. Trans. London, 183 A. (1892), 629; Proc. Roy. Soc. London, 47 (1890), 180; Ber. 23 (1890), R. 361; Bul. soc. chim. [3], 4 (1890), 824; Chem. Centrbl. 1890, i, 669; Chem. News, 61 (1890), 111; J. Chem. Soc. 58 (1890), 947; J. Soc. Chem. Ind. 9 (1890), 624.
- 1890: 43. W. H. WAHL. On the electrodeposition of platinum. Pt.  
J. Frank. Inst. 130 (1890), 62; Chem. News, 62 (1890), 33, 40; Chem. Centrbl. 1890, ii, 360; Ztsch. angew. Chem. 1890, 455; J. Soc. Chem. Ind. 9 (1890), 867.
- 1890: 44. L. N. P. POLAND. Iridiumfaden für Glühlampen. Ir.  
Electrotech. Ztsch. 1890, Aug. 29; Dingl. pol. J. 278 (1890), 46.

- 1890: 45. E. H. GRIFFITHS. On the determination of some boiling and freezing points by means of the platinum thermometer. Pt.  
Phil. Trans. London, 182 A. (1891), 43; Proc. Roy. Soc. London, 48 (1890), 220; J. Chem. Soc. 60 (1891), 251.
- 1890: 46. H. L. CALLENDAR and E. H. GRIFFITHS. On the determination of the boiling point of sulphur and on a method of standardising platinum resistance thermometers by reference to it. Pt.  
Phil. Trans. London, 182 A. (1891), 119; Chem. Centrbl. 1891, ii, 252; Chem. News, 63 (1891), 1; J. Chem. Soc. 60 (1891), 1146; Ztsch. physik. Chem. 7 (1891), 332; Ztsch. anal. Chem. 31 (1892), 549.
- 1890: 47. R. E. LIESEGANG. (Platinum metals in photography.) Pt, Ir, Pd, Os.  
Photog. Archiv, 31 (1890), 170; Dingl. pol. J. 283 (1892), 19; Chem. Ztg. 14 (1890), Rep. 270.
- 1890: 48. F. P. PERKINS. Note on the displacement of silver by platinum and palladium (in toning photographs). Pt, Pd.  
Chem. News, 61 (1890), 87; Chem. Centrbl. 1890, i, 577.
- 1890: 49. L. CLARK. "Platinum toning," London, 1890. Pt.  
Dingl. pol. J. 283 (1892), 18.
- 1890: 50. GASTEIN. (Platinum in photography.) Pt.  
Bul. soc. franç. photog. 1890, 21; Dingl. pol. J. 283 (1892), 19.
- 1890: 51. ————. Ein neues Platintonsalz. Pt.  
Photog. Archiv, 31 (1890), 33; Chem. Centrbl. 1890, i, 552.
- 1890: 52. LENHARD. (Platinum in photography.) Pt.  
Photog. Corresp. 1890, 107; Dingl. pol. J. 283 (1892), 19.
- 1890: 53. MASSE. (Platinum in photography.) Pt.  
Photog. Nachr. 1890, 165; from La Nature; Dingl. pol. J. 283 (1892), 18.
- 1890: 54. BLANCHARD. (Platinum in photography.) Pt.  
Photog. Rundsch. 1890, 22; Dingl. pol. J. 283 (1892), 18.
- 1890: 55. HARRISON. (Platinum in photography.) Pt.  
Bul. assoc. Belge photog. 1890, 523; Dingl. pol. J. 283 (1892), 19.
- 1890: 56. ————. Neues Platintonverfahren. Pt.  
Phot. Mittheil. 26 (1890), 323; Chem. Ztg. 14 (1890), Rep. 122.
- 1890: 57. C. BERTHIOT. (Iridium in photography.) Ir.  
Photog. Notizen, 1890, No. 309; Dingl. pol. J. 283 (1892), 18.
- 1890: 58. ————. (Iridium chlorid paper in photography.) Ir.  
Phot. Mittheil. 27 (1890), 139; Chem. Ztg. 14 (1890), Rep. 270.

- 1890: 59. J. ELSTER and H. GEITEL. Ueber Ozonbildung an glühenden Platinflächen. Pt.  
Ann. der Phys. (Pogg.) [2], 39 (1890), 321; J. Chem. Soc. 58 (1890), 676; Phil. Mag. [5], 29 (1890), 376.
- 1890: 60. L. ARONS. Beobachtungen an elektrischpolarisirten Platinspiegeln. Pt.  
Sitzber. Akad. Berlin, 1890, 969; Ann. der Phys. (Pogg.) [2], 41 (1890), 473; Ztsch. physik. Chem. 6 (1890), 287.
- 1890: 61. T. ARGYROPOULOS. Oscillationen eines weissglühenden Platindrahts durch wiederholte Stromunterbrechungen. Pt.  
Ann. der Phys. (Pogg.) [2], 41 (1890), 503.
- 1890: 62. H. LE CHATELIER. Sur la résistance électrique des métaux. (Platinum and platinum-rhodium.) Pt, Rh.  
C. R. 111 (1890), 454; Dingl. pol. J. 280 (1891), 23; J. Chem. Soc. 60 (1891), 5.
- 1890: 63. F. RICHARZ. Ueber die galvanische Polarisation von Platinelektroden in verdünnter Schwefelsäure. Pt.  
Ann. der Phys. (Pogg.) [2], 39 (1890), 67, 201; J. Chem. Soc. 58 (1890), 551, 676; Ztsch. physik. Chem. 5 (1890), 284.
- 1891: 1. R. HELMHACKER. Ueber das Vorkommen und die Production des Platins am Ural. Pt.  
Berg und Hütten Ztg. 50 (1891), 157; Ztsch. angew. Chem. 1891, 301.
- 1891: 2. ————. Production des Platins in Russland, 1881-1886. Pt, Pd, Ir, Rh, Os, Ru.  
Chem. Indust. 14 (1891), 15.
- 1891: 3. K. SEUBERT. Die Atomgewichte der Platinmetalle. (Ru, 101.4; Rh, 102.7; Pd, 106.35; Os, 190.3; Ir, 192.5; Pt, 194.3; O = 15.96.) Pt, Pd, Ir, Rh, Os, Ru.  
Ann. Chem. (Liebig), 261 (1891), 272; Ber. 24 (1891), R. 260; Bul. soc. chim. [3], 7 (1892), 50; Chem. Centrbl. 1891, i, 492; J. Chem. Soc. 60 (1891), 885; Ztsch. angew. Chem. 1891, 148; Chem. Ztg. 15 (1891), Rep. 65; Ztsch. anal. Chem. 30 (1891), 756.
- 1891: 4. K. SEUBERT. Ueber das Atomgewicht des Osmiums (190.3, O = 15.96). Os.  
Ann. Chem. (Liebig), 261 (1891), 257; Ber. 24 (1891), R. 259; Bul. soc. chim. [3], 7 (1892), 50; Chem. Centrbl. 1891, i, 492; J. Chem. Soc. 60 (1891), 884; J. anal. Chem. (Hart), 5 (1891), 221; Chem. Ztg. 15 (1891), Rep. 65.

- 1891: 5. L. PIGEON. Sur deux nouvelles combinaisons cristallisées du chlorure platinique avec l'acide chlorhydrique. Pt.  
C. R. 112 (1891), 1218; Ber. 24 (1891), R. 592; Bul. soc. chim. [3], 6 (1891), 548; Chem. News, 63 (1891), 284; J. Chem. Soc. 60 (1891), 1325; J. Russ. Chem. Soc. 23, ii (1891), 159; Chem. Ztg. 15 (1891), Rep. 161.
- 1891: 6. M. VÈZES. Sur les sels bromoazotés et iodoazotés du platine. (Bromo- and iodo-nitrates.) Pt.  
C. R. 112 (1891), 616; 113 (1891), 696; Bul. soc. chim. [3], 6 (1891), 175; 7 (1892), 148; Ber. 24 (1891), R. 348; 25 (1892), R. 3; Chem. Centrbl. 1891, i, 782; 1892, i, 152; Chem. News, 63 (1891), 177; 64 (1891), 284; J. Chem. Soc. 60 (1891), 807; 62 (1892), 280.
- 1891: 7. I. GUARESCHI. (Platinum thiocyanates.) Pt.  
Giorn. Accad. Med. 1891; Chem. Centrbl. 1891, ii, 620; J. Chem. Soc. 62 (1892), 286.
- 1891: 8. A. ROSENHEIM. Ueber die Einwirkung von Platinoxidhydrat auf wolframsaure Salze. Pt.  
Ber. 24 (1891), 2397; Bul. soc. chim. [3], 7 (1892), 67; Chem. Centrbl. 1891, ii, 454; J. Chem. Soc. 60 (1891), 1323.
- 1891: 9. R. SCHNEIDER. Ueber zwei neue Selenosalze. (Seleno-platinostannates.) Pt.  
J. prakt. Chem. [2], 44 (1891), 507; Bul. soc. chim. [3], 8 (1892), 682; Chem. Centrbl. 1892, i, 151; J. Chem. Soc. 62 (1892), 281.
- 1891: 10. F. MYLIUS and F. FOERSTER. Ueber die Verbindungen des Kohlenoxydplatins. Pt.  
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- 1892: 12. M. VÈZES. Sur les sels azotés du platine. (Nitrites.) Pt. C. R. 115 (1892), 44; Ann. chim. phys. [6], 29 (1893), 145; Ber. 25 R. (1892), 714; Bul. soc. chim. [3], 7 (1892), 664; Chem. Centrbl. 1892, ii, 315; Chem. News, 66 (1892), 61; J. Chem. Soc. 62 (1892), 1283; Ztsch. anorg. Chem. 2 (1892), 272.
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- 1892: 22. L. BALBIANO. Sopra i composti plato-pirrazolici. Pt.  
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## 1. HISTORY.

- 1806: 3 Fourcroy and Vauquelin  
1850: 5 Thomson

### Platinum.

- 1814: 1 Vauquelin  
1845: 2 Schweigger  
1860: 18 Delarue

### Platinum in Russia.

- 1827: 1 Mamyscheff  
1880: 1 Köppen

### Rhodium as iron.

- 1841: 6 Tilley

### Platinum known to the ancients.

- 1790: 1 Cortenovis  
1845: 1 Schubarth  
1850: 1 Paravey

## 2. DISCOVERY (see also New Metals, 3).

### Platinum.

- 1751: 1 Watson  
1755: 1 Lewis  
1758: 1 M....  
1758: 2 Macquer  
1805: 6 Collet-Descotils  
1805: 7 Tilloch  
1880: 1 Köppen

### Palladium.

- 1803: 1 Chenivix  
1803: 2 Chenivix  
1803: 3 Chenivix  
1803: 4 —————  
1803: 5 —————  
1803: 6 Richter  
1803: 7 Rose and Gehlen  
1803: 8 Vauquelin  
1804: 1 Chenivix  
1804: 2 Chenivix  
1804: 3 —————  
1804: 4 Hume  
1804: 5 Trommsdorff  
1804: 6 Mussin-Puschkin  
1804: 7 Mussin-Puschkin

- 1805: 2 Wollaston  
1805: 3 Wollaston  
1805: 4 —————  
1805: 5 [Berthollet]  
1805: 9 Gilbert  
1805: 11 [Gehlen]  
1805: 12 Gehlen  
1806: 5 Gilbert

### Rhodium.

- 1804: 11 Collet-Descotils  
1804: 13 Wollaston  
1805: 6 Collet-Descotils  
1805: 7 Tilloch  
1805: 9 Gilbert  
1805: 11 [Gehlen]

### Iridium.

- 1804: 12 Tennant  
1805: 9 Gilbert  
1805: 10 [Gilbert]  
1805: 11 [Gehlen]

### Osmium.

- 1804: 12 Tennant  
1805: 9 Gilbert  
1805: 10 [Gilbert]  
1805: 11 [Gehlen]

### Ruthenium.

- 1844: 4 Claus  
1844: 5 Claus

### Platinum as alloy of gold and iron.

- 1774: 1 Buffon  
1774: 2 Blondeau  
1784: 3 Buffon  
1784: 4 Milly  
1786: 3 Morveau

### Palladium as platinum amalgam.

- 1803: 1 Chenivix  
1808: 1 Collet-Descotils  
1808: 2 Berthollet

## 3. NEW METALS in platinum ore.

### Iridium.

- 1803: 9 Fourcroy and Vauquelin  
1803: 10 Collet-Descotils  
1804: 8 Fourcroy and Vauquelin

**Rhodium.**

- 1804: 9 Fourcroy  
1804: 10 Fourcroy

**Ruthenium (I), Polinium and Pluranium.**

- 1826: 5 Osann  
1829: 6 Osann  
1845: 5 Claus  
1845: 6 Osann  
1845: 7 Osann  
1845: 8 Claus  
1845: 9 Frémy

**Ruthenium.**

- 1844: 4 Claus  
1844: 5 Claus  
1845: 5 Claus  
1845: 6 Osann  
1845: 7 Osann  
1845: 8 Claus  
1845: 9 Frémy

**Unnamed (California).**

- 1852: 3 Genth

**Unnamed (Oregon).**

- 1862: 2 Chandler

**Davyum.**

- 1877: 3 Kern  
1877: 4 Allen

**Uralium.**

- 1879: 3 Guyard

**Unnamed (Russia).**

- 1883: 2 Wilm

**4. OCCURRENCE.**

- 1806: 2 Bucholz  
1823: 1 C. C.  
1826: 3 Menge  
1827: 5 Humboldt  
1828: 5 ———  
1842: 5 ———  
1847: 5 Pettenkofer  
1854: 3 ———  
1870: 37 Skey  
1877: 1 ———  
1879: 2 Jeremejew  
1880: 2 Newberry  
1890: 1 Blömeke

**In South America.**

- 1748: 1 Ulloa  
1751: 1 Watson

- 1755: 1 Lewis  
1788: 1 Celis  
1792: 1 Bergman  
1793: 1 Haüy  
1802: 1 Thomson  
1809: 1 Wollaston  
1811: 1 Gehlen  
1817: 1 Humboldt  
1818: 2 Mawe  
1821: 1 ———  
1825: 1 Humboldt  
1826: 1 Humboldt  
1833: 7 Lampadius and Plattner  
1856: 1 Boussingault  
1861: 4 Damour  
1882: 2 Seamon

**In San Domingo.**

- 1810: 1 Morveau  
1810: 2 Percy  
1811: 1 Gehlen  
1873: 1 Vogel

**In Mexico.**

- 1811: 2 Humboldt  
1874: 1 Burkart  
1875: 4 Sandberger  
1876: 3 Uslar

**In United States.**

- 1850: 3 Patterson

**California.**

- 1849: 2 ———  
1850: 4 Teschemacher  
1852: 2 Genth  
1859: 3 Weil  
1862: 1 Ludwig  
1879: 1 Luthy

**Oregon.**

- 1854: 1 Blake

**New York.**

- 1881: 2 Collier

**Pennsylvania.**

- 1851: 2 Genth

**North Carolina.**

- 1847: 4 Shepard  
1881: 1 Hidden  
1892: 1 Venable

**Missouri.**

- 1859: 2 ———

## In Canada.

- 1851: 1 Hunt
- 1886: 1 Hoffman
- 1887: 1 Dawson
- 1889: 2 Clarke and Catlett
- 1889: 3 Hoffman
- 1890: 3 ———
- 1892: 4 ———
- 1893: 4 Donald

## In Russia.

- 1826: 1 Humboldt
- 1826: 2 ———
- 1827: 2 Kupffer
- 1827: 3 ———
- 1827: 4 ———
- 1828: 1 Engelhardt
- 1828: 2 F. H.
- 1828: 3 ———
- 1828: 4 Marx
- 1829: 1 Kupffer
- 1829: 2 ———
- 1829: 3 ———
- 1830: 1 Engelhardt
- 1831: 1 ———
- 1831: 2 Fuchs
- 1833: 2 ———
- 1835: 1 ———
- 1835: 2 Teploff
- 1842: 2 Menge
- 1842: 3 ———
- 1843: 1 Humboldt
- 1843: 2 ———
- 1844: 1 Leplay
- 1846: 1 Murchison
- 1859: 4 Haidinger
- 1874: 2 Frenzel
- 1877: 2 Kern
- 1881: 3 ———
- 1884: 1 ———
- 1890: 2 Laurent
- 1891: 1 Helmhacker
- 1893: 1 ———
- 1894: 3 ———
- 1894: 4 ———
- 1895: 1 Inostranzeff
- 1895: 2 Muschkjetoff

## In Lapland.

- 1870: 1 Nordenskjöld

## In France.

- 1833: 3 Claubry
- 1833: 4 Dangaz
- 1833: 5 D'Argy
- 1834: 1 Berthier and Becquerel
- 1834: 2 Villain

1834: 3 ———

1849: 1 Ebelmen

## In Spain.

- 1806: 1 Vanquelin
- 1818: 1 Heuland

## In Rhinesand.

- 1835: 4 Hopff
- 1841: 1 Döbereiner
- 1841: 2 F. D. H.

## In Harz Mts.

- 1835: 3 Berzelius

## In Siebengebirgen.

- 1854: 4 ———

## In Alps.

- 1848: 1 Gueymard

## In Hungary.

- 1847: 2 Molnár
- 1847: 3 Kopetzky and Patera

## In Scotland.

- 1869: 1 ———

## In Ireland.

- 1850: 2 Mallet

## In Borneo.

- 1839: 2 Horner
- 1855: 1 Bocking
- 1858: 1 Bleekrode
- 1859: 1 Bleekrode

## In Ava.

- 1833: 6 Prinsep

## In Burmah.

- 1848: 2 Faber

## In Australia.

- 1896: 1 ———

## In Algiers.

- 1838: 1 Aimé

## In meteorites.

- 1835: 7 Osann

## In the sun.

- 1878: 49 Lockyer
- 1887: 2 Hutchins and Holden

## With silver.

- 1836: 2 Herberger
- 1837: 1 Pettenkofer
- 1848: 3 Pettenkofer
- 1848: 4 Plattner

- 1852: 4 Palmstedt  
 1875: 6 ———  
 1876: 4 Rössler
- With gold.  
 1849: 9 Pettenkofer  
 1887: 3 Martin (in bullion)
- With copper.  
 1847: 1 Leuchtenberg
- Magnetic ores.  
 1866: 1 Kokshearow  
 1875: 27 Daubrée  
 1876: 1 Terreil  
 1883: 1a Wilm
- Sperrylite, in Canada.  
 1889: 1 Wells and Penfield  
 1889: 3 Hoffman  
 1896: 2 Walker
- Nickel in platinum.  
 1876: 2 Daubrée
- Barium in platinum.  
 1865: 1 Kraut
- PALLADIUM.
- In Brazil.  
 1825: 1 Humboldt  
 1837: 2 Johnson and Lampadius  
 1837: 4 Fellenberg  
 1882: 3 Seamon  
 1882: 4 Mallet
- In Germany.  
 1829: 4 Zincken  
 1829: 5 Benecke and Rienecker  
 (Harz Mts.)
- In Caucasus.  
 1893: 5 Wilm
- In meteorites.  
 1890: 5 Trottarelli
- With silver.  
 1875: 6 ———  
 1876: 4 Rössler
- IRIDIUM.  
 1835: 6 Rose
- In California.  
 1854: 2 Dubois
- In Canada.
- OSMIRIDIUM.  
 1835: 11 Döbereiner
- In Russia.  
 1833: 1 Rose  
 1882: 1 Lasaulx
- In United States.  
 1850: 3 Patterson  
 1852: 2 Genth (Cal.)  
 1861: 1 Torrey (Cal.)
- In Canada.  
 1851: 1 Hunt  
 1887: 1 Dawson  
 1889: 3 Hoffman
- With gold.  
 1839: 3 Wöhler  
 1843: 3 Weinlig  
 1887: 3 Martin
- IRITE.  
 1836: 1 Hermann  
 1841: 3 Hermann  
 1851: 3 Kenngott
- OSMITE.  
 1836: 1 Hermann
- RUTHENIUM and OSMIUM. Laurite.  
 1866: 2 Wöhler (Borneo)  
 1869: 2 Wöhler (Oregon)
- MATRIX of platinum.  
 1830: 2 Engelhardt  
 1839: 1 Rose  
 1857: 1 Damour and Descloizeaux  
 1894: 2 Meunier
- In Russia.  
 1834: 4 Rose  
 1875: 1 Descloizeaux  
 1875: 2 Daubrée  
 1893: 2 Daubrée  
 1893: 3 Inostranzeff  
 1894: 1 Inostranzeff
- In Alps.  
 1861: 3 Gueymard
5. COMPOSITION OF ORES.  
 1829: 6 Osann  
 1835: 9 Döbereiner  
 1842: 6 Svanberg  
 1844: 4 Claus  
 1844: 5 Claus  
 1845: 7 Osann  
 1885: 2 Wilm

## From Russia.

- 1825: 2 Laugier  
 1825: 3 Laugier  
 1826: 4 Breithaupt  
 1826: 5 Osann  
 1844: 2 Kositzky  
 1876: 1 Terreil

## From France.

- 1833: 4 Dangaz

## From Alps.

- 1852: 1 Gueymard

## From South America.

- 1834: 6 Svanberg  
 1835: 5 Berzelius

## From San Domingo.

- 1810: 3 Vauquelin

## From Canada.

- 1886: 1 Hoffman

## Iridium ores.

- 1826: 6 Thomson

## 6. PRODUCTION.

- 1828: 7 Breithaupt  
 1830: 4 Humboldt  
 1835: 8 —————  
 1843: 4 —————  
 1874: 5 —————  
 1890: 6 —————  
 1893: 6 [Raymond]  
 1893: 7 —————  
 1894: 3 —————  
 1894: 4 —————  
 1894: 5 Helmhacker  
 1894: 6 Keppen

## In Russia.

- 1832: 1 —————  
 1841: 4 —————  
 1842: 1 Rose  
 1842: 4 —————  
 1845: 3 J. A.  
 1845: 4 —————  
 1849: 3 —————  
 1852: 5 —————  
 1860: 3 —————  
 1862: 3 Jossa  
 1862: 4 Jossa  
 1871: 1 —————  
 1873: 4 Raymond  
 1876: 5 Frantz  
 1876: 6 Brachelli  
 1885: 1 Katterfeld  
 1888: 1 Kulibin

- 1889: 4 —————  
 1890: 2 Lauren<sup>t</sup>  
 1890: 4 —————  
 1890: 6 —————  
 1891: 1 Helmhacker  
 1891: 2 —————  
 1892: 2 —————

## Robbery.

- 1890: 7 —————

## 7. PRICE.

- 1834: 5 Cooke  
 1857: 2 —————  
 1857: 19 Heraeus  
 1876: 7 —————  
 1892: 3 —————  
 1892: 5 —————

## Palladium.

- 1823: 2 Puymaurin

## Osmiridium.

- 1831: 3 —————

## 8. GENERAL TREATISES.

- 1805: 3 Wollaston  
 1806: 4 Trommsdorff  
 1828: 9 Berzelius  
 1829: 9 Berzelius  
 1854: 6 Claus  
 1855: 3 Frémy  
 1859: 8 Claus  
 1859: 9 Deville and Debray  
 1861: 5 Faraday  
 1861: 6 Gibbs  
 1866: 5 Forster  
 1878: 1 Phillipp  
 1878: 2 —————  
 1883: 1 Claus

## On platinum.

- 1758: 1 M.  
 1758: 2 Macquer  
 1780: 1 Bergman  
 1782: 1 von Sickingen  
 1799: 1 Proust  
 1801: 1 Proust  
 1803: 9 Fourcroy and Vauquelin  
 1842: 8 Kane  
 1881: 5 Wilm

## On palladium.

- 1813: 1 Vauquelin  
 1814: 2 Vauquelin  
 1827: 13 Fischer  
 1842: 8 Kane  
 1843: 6 Cock  
 1847: 11 Fischer

## On iridium.

- 1814: 1 Vauquelin  
 1854: 8 Uricoechea  
 1877: 21 Debray  
 1885: 23 Perry

## On rhodium.

- 1813: 1 Vauquelin  
 1814: 2 Vauquelin  
 1868: 1 Bunsen

## On osmium.

- 1814: 1 Vauquelin  
 1833: 9 Berzelius  
 1833: 11 Breithaupt  
 1844: 8 Frémy  
 1859: 11 Eichler  
 1863: 3 Jacobi  
 1866: 9 Wöhler  
 1876: 10 Deville and Debray

## On ruthenium.

- 1846: 7 Claus  
 1876: 11 Deville and Debray

## 9. DECOMPOSITION OF ORES.

- 1804: 8 Fourcroy and Vauquelin  
 1804: 9 Fourcroy  
 1804: 14 Tennant and Wollaston  
 1807: 1 Collet-Descotils  
 1827: 6 Arkhipoff  
 1834: 8 Wöhler  
 1835: 10 Joss  
 1846: 2 Fritzsche  
 1847: 6 Hess  
 1854: 5 Frémy  
 1860: 5 Deville and Debray  
 1873: 2 Knösel  
 1883: 3 Wilm  
 1885: 2 Wilm

## 10. SEPARATION AND PURIFICATION OF METALS.

- 1834: 9 Persoz  
 1857: 3 Deville and Debray  
 1857: 4 Mucklé and Wöhler  
 1860: 5 Deville and Debray  
 1862: 7 Deville and Debray  
 1863: 2 Guyard  
 1864: 1 Lea  
 1872: 1 Bettendorff  
 1876: 9 Phillip  
 1878: 3 Matthey  
 1879: 4 Matthey  
 1885: 2 Wilm  
 1891: 31 Joly and Leidié

## Platinum.

- 1798: 4 Mussin-Puschkin  
 1816: 1 Ridolfi  
 1818: 3 Cloud  
 1822: 1 Barruel  
 1834: 7 Sobolevsky  
 1836: 17 Liebig  
 1838: 3 Döbereiner  
 1841: 2 F. D. H.  
 1866: 7 Birnbaum  
 1867: 7 Schneider  
 1868: 11 Chalmers and Tatlock  
 1875: 9 Wagner  
 1876: 8 ———  
 1877: 6 Opificius  
 1879: 49 Gladstone and Tribe  
 1880: 3 Wilm  
 1881: 32 ———  
 1886: 2 Noad  
 1892: 26 Mylius and Foerster  
 1892: 27 Mylius and Foerster  
 1892: 47 Warren

## Palladium.

- 1818: 4 Accum  
 1829: 7 Wollaston  
 1835: 9 Döbereiner  
 1843: 5 Lassaigue  
 1881: 5 Wilm

## Iridium.

- 1830: 5 Quesneville  
 1833: 8 Wöhler  
 1833: 12 Persoz  
 1837: 3 Frick  
 1844: 3 Kositzky  
 1855: 5 Hennin  
 1866: 7 Birnbaum  
 1867: 3 Schneider  
 1874: 6 Deville, Debray and Morin  
 1879: 5 Jungfleisch  
 1883: 29 Dudley

## Osmium.

- 1814: 3 Laugier  
 1829: 8 Wollaston  
 1830: 5 Quesneville  
 1833: 8 Wöhler  
 1833: 12 Persoz  
 1838: 9 Ellet

## 11. REDUCTION TO METAL.

- 1821: 13 Clarke

## Platinum.

- 1827: 15 Fischer  
 1829: 14 Kastner

1829: 19 Fischer  
 1830: 10 Wach  
 1831: 8 Döbereiner  
 1833: 14 Phillips  
 1835: 12 Döbereiner  
 1835: 13 Joss  
 1840: 6 Parisot  
 1841: 14 Böttger  
 1847: 20 Kessler  
 1858: 8 Hempel  
 1861: 16 Béchamp and Saint  
       Pierre  
 1861: 17 Faget  
 1861: 18 Saint-Pierre  
 1862: 14 Saint-Pierre  
 1862: 15 Personne  
 1864: 5 Böttger  
 1864: 7 Brunner  
 1872: 18 Böttger  
 1873: 12 Russell  
 1875: 23 Lossen  
 1877: 24 ———  
 1882: 24 Post  
 1893: 37 Bornträger  
 1895: 28 Vitali  
 1895: 29 Stiebel

#### Palladium.

1850: 10 Reynoso  
 1862: 14 Saint-Pierre  
 1862: 15 Personne  
 1864: 7 Brunner  
 1872: 18 Böttger  
 1873: 12 Russell  
 1895: 28 Vitali

#### Iridium.

1864: 7 Brunner

#### Osmium.

1893: 36 Gulewitsch

### 12. PLATINUM SPONGE; preparation.

1826: 10 Döbereiner  
 1826: 13 Döbereiner  
 1829: 21 Planíavá  
 1830: 12 Kastner  
 1830: 13 Faraday  
 1833: 23 Böttger  
 1844: 18 Hirschberg  
 1858: 14 Brunner  
 1874: 29 Vulpius  
 1890: 32 Loew

#### Platinum black.

1800: 6 Henry  
 1804: 17 Proust

1829: 22 Liebig  
 1832: 3 Döbereiner  
 1832: 11 Döbereiner  
 1832: 14 ———  
 1834: 18 Bley  
 1835: 9 Döbereiner  
 1835: 12 Döbereiner  
 1836: 8 Döbereiner  
 1836: 9 Döbereiner  
 1858: 8 Hempel  
 1872: 15 Smith  
 1876: 55 Zdrawkowitch  
 1877: 37 Böttger  
 1882: 18 Mulder and van der  
       Meulen  
 1886: 36 Drechsel

### 13. ATOMIC WEIGHTS.

1818: 7 Berzelius  
 1827: 7 ———  
 1828: 9 Berzelius  
 1833: 13 Berzelius  
 1834: 14 Berzelius  
 1835: 18 Berzelius  
 1846: 17 Playfair and Joule  
 1869: 3 Watts  
 1880: 2a Becker  
 1881: 16 Clarke  
 1882: 12 Clarke  
 1883: 14 Meyer and Seubert  
 1884: 8 Clarke  
 1886: 10 van der Plaats  
 1891: 3 Seubert  
 1896: 3 Clarke

#### Platinum.

1828: 9 Berzelius  
 1852: 9 Andrews  
 1881: 9 Seubert  
 1882: 23 Fresenius  
 1884: 7 Halberstadt  
 1888: 2 Seubert  
 1881: 17 Dewar and Scott (vapor  
       dens.  $\text{PtCl}_2$ )  
 1890: 28 Heycock and Neville  
       (mol. wt. in tin)

#### Palladium.

1828: 9 Berzelius  
 1847: 4a Icilus  
 1889: 5 Keiser  
 1892: 24 Bailey and Lamb  
 1892: 24 Keller and Smith  
 1893: 28 Joly and Leidié  
 1894: 18 Keiser and Breed  
 1894: 20 Clarke



## Iridium.

- 1826: 6 Thomson  
1828: 9 Berzelius  
1878: 11 Seubert  
1890: 20 Joly

## Rhodium.

- 1828: 9 Berzelius  
1853: 5 Schneider  
1883: 13 Jörgensen  
1890: 9 Seubert and Kobbé

## Osmium.

- 1828: 9 Berzelius  
1844: 8 Frémy  
1853: 5 Schneider  
1857: 3 Deville and Debray  
1888: 3 Seubert  
1891: 4 Seubert

## Ruthenium.

- 1844: 4 Claus  
1888: 14 Joly  
1889: 10 Joly

## 14. COMPOUNDS.

## GENERAL TREATISES.

- 1894: 7 Erdmann

## Platinum.

- 1812: 3 Davy  
1817: 2 Vauquelin  
1820: 1 Davy  
1886: 3 Prost

## Rhodium.

- 1888: 12 Leidié  
1890: 10 Seubert and Kobbé

## Osmium.

- 1893: 10 Moraht and Wischin

## 15. OXIDS.

- 1868: 7 Wöhler  
1878: 4 Deville and Debray

## Platinum.

- 1802: 2 Cuthbertson  
1812: 4 Berzelius  
1813: 8 Vogel  
1817: 14 Cooper  
1820: 4 Rose  
1821: 2 Berzelius  
1821: 5 Thomson  
1826: 10 Döbereiner  
1830: 6 Berzelius  
1830: 7 Liebig  
1832: 2 Herschel  
1832: 3 Döbereiner

1833: 15 Döbereiner

1833: 21 Göbel

1835: 11 Döbereiner

1838: 2 De la Rive

1841: 7 Wittstein

1841: 8 De la Rive

1842: 13 Schönbein

1844: 9 Schaffner

1846: 4 Osann

1847: 19 Hittorf

1868: 9 Topsöe

1870: 10 Frémy

1870: 18 Johannsen

1875: 15 Delachanel and Mermet

1876: 28 Skey

1876: 29 Skey

1877: 9 Jörgensen

1882: 16 Wilm

1887: 29 Reinhardt

1889: 7 Rousseau

1891: 22 Kwasnik

## Palladium.

1813: 8 Vogel

1826: 9 Miller

1829: 18 Fischer

1833: 21 Göbel

1869: 14 Schneider

1874: 19 Wöhler

1892: 9 Wilm

## Iridium.

1847: 9 Claus

1890: 11 Geisenheimer

## Rhodium.

1818: 6 Berzelius

## Osmium.

1844: 7 Frémy

1846: 9 Svanberg

1860: 10 Mallet

1892: 46 Kolossow

## Ruthenium.

1875: 18 Deville and Debray

1888: 13 Debray and Joly

1890: 35 Dufet

1891: 16 Joly

1891: 17 Joly

## 16. SULFIDS.

1840: 3 Fellenberg

## Platinum.

1812: 2 Davy

1812: 4 Berzelius

1813: 8 Vogel

1821: 3 Berzelius  
 1825: 6 Berzelius  
 1834: 10 Böttger  
 1838: 10 Reinsch  
 1846: 14 Crosnier  
 1860: 8 Schiff  
 1864: 14 Pisko  
 1869: 13 Schneider  
 1869: 14 Schneider  
 1872: 8 Guerout  
 1873: 8 Schneider  
 1874: 23 Schneider  
 1877: 10 Ribau  
 1877: 11 von Meyer  
 1879: 28 de Clermont  
 1879: 29 de Clermont and Frommel  
 1892: 14 Schneider  
 1893: 17 Schneider  
 1894: 29 Schiff and Tarugi  
 1895: 8 Roessler  
 1896: 10 Antony and Lucchesi  
 1896: 15 Durkee (thioplatingates)

#### Palladium.

1813: 8 Vogel  
 1869: 14 Schneider  
 1873: 9 Schneider  
 1874: 23 Schneider  
 1893: 16 Petrenko-Kritschenko  
 1895: 8 Roessler

#### Iridium.

1834: 10 Böttger  
 1893: 14 Antony  
 1893: 15 Antony

#### Rhodium.

1821: 3 Berzelius  
 1883: 6 Debray

#### Osmium.

1877: 12 von Meyer

#### SELENIDS.

1818: 5 Berzelius  
 1830: 9a ——— (palladium)  
 1895: 8 Roessler

### 17. HALOGEN COMPOUNDS.

1888: 24 Hampe  
 1889: 6 Pigeon  
 1893: 22 Werner

#### PLATINUM CHLORIDES.

1782: 2 Wenzel  
 1783: 1 de l'Isle

1797: 1 Mussin-Puschkin  
 1800: 1 Mussin-Puschkin  
 1803: 10 Collet-Descotils  
 1804: 15 Mussin-Puschkin  
 1804: 16 Mussin-Puschkin  
 1817: 3 Vauquelin  
 1821: 7 Murray  
 1827: 9 van Mons  
 1827: 10 Bonsdorff  
 1827: 11 ———  
 1828: 10 Bonsdorff  
 1828: 25 Fischer  
 1829: 10 Zeise  
 1830: 8 Hünefeld  
 1834: 11 Kane  
 1834: 16 Kastner  
 1835: 12 Döbereiner  
 1835: 14 Mather  
 1835: 16 Kane  
 1836: 3 Hermann  
 1838: 3 Döbereiner  
 1843: 8 Gerhardt  
 1846: 12 Rose  
 1850: 6 Frémy  
 1850: 7 Wurtz  
 1851: 5 Claudet  
 1851: 6 Landolt  
 1854: 10 Williams  
 1854: 11 Gladstone (optical)  
 1854: 15 Schabus (cryst.)  
 1854: 18 Graham  
 1855: 7 Löwig  
 1855: 8 Anderson  
 1855: 9 Wurtz  
 1855: 16 Weltzien (cryst.)  
 1855: 17 Marignac (cryst.)  
 1856: 2 Scheibler  
 1856: 3 Salm-Horstmar  
 1856: 4 Hofmann and Cahours  
 1856: 11 Gibbs and Genth  
 1857: 9 Hofmann  
 1857: 14 Descloizeaux (cryst.)  
 1858: 4 Williams  
 1859: 15 Knop  
 1860: 7 Boedeker  
 1860: 9 Klippel  
 1860: 11 Hofmann  
 1861: 2 Sella  
 1861: 7 Kirchhoff and Bunsen  
 1861: 8 Holzmann  
 1861: 10 Lang  
 1861: 15 Cleve  
 1862: 11 Baudrimont  
 1862: 13 Braun  
 1863: 4 Böttger  
 1863: 5 Millon and Commaille

- 1864: 8 Schrötter  
 1864: 9 Crookes  
 1864: 10 Crookes  
 1864: 13 Kopp  
 1865: 2 Zepharovitch (cryst.)  
 1865: 3 Cleve  
 1866: 16 Commaille  
 1867: 4 Birnbaum  
 1867: 6 Weber  
 1868: 8 Topsøe  
 1869: 26 Riemann (as indelible ink)  
 1870: 3 Norton  
 1870: 4 Thomsen  
 1870: 32 Thomsen (thermo-chem.)  
 1871: 6 Lawrow  
 1871: 19 Topsøe and Christiansen (cryst. and opt.)  
 1871: 21 Thomsen (thermo-chem.)  
 1872: 3 Norton  
 1873: 5 Marignac  
 1873: 6 Welkow  
 1873: 7 Gibbs  
 1873: 30 Schröder  
 1874: 13 Thomsen  
 1874: 16 Welkow  
 1874: 18 Cleve  
 1874: 24 Jolin  
 1874: 31 Topsøe (cryst.)  
 1874: 41 Topsøe (cryst.)  
 1875: 13 Godeffroy  
 1875: 24 Meyer and Locher  
 1876: 12 Nilson  
 1876: 13 Nilson  
 1877: 14 Calhours  
 1877: 42 Clarke  
 1878: 6 Jörgensen  
 1878: 7 Frerichs and Smith  
 1878: 8 Cleve  
 1878: 13 Nilson and Petterson  
 1878: 20 Böttger  
 1878: 30 Clarke  
 1878: 43 Thomsen (thermo-chem.)  
 1879: 9 Heintz  
 1879: 10 Jörgensen  
 1879: 17 Reinitzer  
 1879: 18 Seelheim  
 1879: 19 Meyer  
 1879: 20 Smith  
 1879: 21 Dunnington  
 1879: 23 Gintl  
 1880: 8 Christensen  
 1880: 13 Cleve  
 1880: 15 Ditte  
 1880: 17 Eder  
 1881: 8 Hesse  
 1881: 13 Clarke and Owens  
 1881: 14 Jörgensen  
 1881: 17 Dewar and Scott  
 1882: 10 Jörgensen  
 1882: 19 Gavazzi  
 1882: 21 Topsøe  
 1883: 12 Cleve  
 1883: 15 Opificius  
 1883: 16 de Conineck  
 1883: 17 Levallois  
 1883: 18 Gove  
 1884: 5 Jörgensen  
 1884: 6 Jörgensen  
 1884: 9 Romanis  
 1884: 10 Raoult  
 1885: 3 Cleve  
 1885: 4 Cleve  
 1885: 5 Jörgensen  
 1886: 12 Foussereau  
 1887: 4 Malbot  
 1887: 5 Jörgensen  
 1887: 8 Semmler  
 1887: 18 Duclaux  
 1887: 52 Miesler  
 1888: 4 Engel  
 1888: 5 Stölba  
 1888: 6 Laird  
 1888: 7 Klinger and Maassen  
 1888: 9 Weibull  
 1888: 23 Gerlach  
 1888: 25 Walden  
 1888: 26 Rüdorff  
 1888: 28 Barfoed  
 1889: 19 Ostwald  
 1890: 27 Pigeon  
 1891: 5 Pigeon  
 1891: 13 Christenen  
 1891: 14 Le Bel  
 1891: 23 Seubert and Schmidt  
 1891: 25 Pigeon (thermo-chem.)  
 1891: 26 Pigeon (thermo-chem.)  
 1892: 7 Pullinger  
 1892: 8 Shenstone and Beck  
 1892: 17 Jörgensen  
 1892: 43 Holleman  
 1892: 44 Pélilot  
 1893: 11 Montemartini  
 1893: 12 Shenstone and Beck  
 1893: 13 Le Bel (cryst.)  
 1893: 33 Lea  
 1894: 8 Lea  
 1894: 10 Pigeon  
 1894: 17 Werner and Miolati

- 1895: 13 Werner  
 1895: 6 Pigeon  
 1895: 27 Soustadt  
 1896: 4 Herty  
 1896: 5 Miolati  
 1896: 6 Hake  
 1896: 7 Smits
- “Nitroso” chlorids.  
 1840: 4 Rogers and Boyé  
 1867: 6 Weber  
 1890: 8 Vèzes
- COMPOUNDS OF PLATINUM CHLORIDS. “Acechlorplatin.”  
 1829: 12 Berzelius  
 1831: 4 Zeise  
 1831: 5 Zeise  
 1834: 13 Liebig  
 1836: 5 Zeise  
 1837: 8 Liebig  
 1838: 8 Zeise  
 1839: 4 Malaguti
- with phosphorus compounds.  
 1870: 5 Cahours and Gal  
 1870: 6 Cahours and Gal  
 1870: 7 Cahours and Gal  
 1870: 8 Kolbe  
 1870: 9 Schützenberger  
 1870: 25 Descloiseaux (cryst.)  
 1872: 4 Schützenberger and  
     Fontaine  
 1872: 5 Saillard  
 1876: 18 Quesneville  
 1878: 9 Cochin  
 1881: 11 Pomey  
 1885: 16 Kulisch  
 1887: 6 Pomey
- with carbon monoxid.  
 1825: 4 Zeise  
 1868: 6 Schützenberger  
 1870: 9 Schützenberger  
 1891: 10 Mylius and Foerster  
 1891: 11 Foerster  
 1891: 12 Pullinger
- with ethylene.  
 1861: 14 Griess and Martius  
 1867: 5 Birnbaum  
 1871: 7 Sadtler
- with ethyl cyanid.  
 1858: 2 Henke  
 1858: 3 Thau
- PLATINUM BROMIDS.  
 1826: 7 Balard  
 1828: 10 Bonsdorff
- 1832: 4 Bonsdorff  
 1868: 8 Topsøe (cryst.)  
 1871: 19 Topsøe and Christian-  
     sen (cryst. and opt.)  
 1874: 41 Topsøe  
 1880: 5 Meyer and Züblin  
 1891: 12 Pullinger  
 1892: 34 Pigeon (thermo-chem.)
- Chloro-bromid.  
 1879: 7 Pitkin
- “Acebromplatin.”  
 1861: 13 Nicklès
- Compound of platinum bromid  
 with ethylene.  
 1870: 22 Chojnacki
- IODIDS.  
 1814: 5 Ruhland  
 1823: 3 Silliman  
 1825: 7 Pleischl  
 1825: 8 Pleischl  
 1829: 13 Lassaigne  
 1832: 5 Lassaigne  
 1832: 6 Lassaigne  
 1832: 7 Orfila  
 1832: 8 Kane  
 1833: 17 Kane  
 1833: 18 Kane  
 1833: 19 Lassaigne  
 1833: 20 Phillips  
 1835: 15 Mather  
 1836: 6 Buchner  
 1855: 6 Clementi  
 1856: 12 Deville  
 1860: 7 Boedeker  
 1868: 8 Topsøe (cryst.)  
 1878: 21 Selmi
- Chloro-iodids.  
 1868: 2 Kämmerer
- FLUORIDS.  
 1823: 4 Berzelius  
 1877: 8 Clarke  
 1885: 9 Moissan  
 1889: 8 Moissan
- PALLADIUM CHLORIDS.  
 1827: 11 ———  
 1828: 10 Bonsdorff  
 1846: 12 Rose  
 1867: 7 Croft  
 1869: 11 Topsøe (cryst.)  
 1874: 14 Welkow  
 1874: 15 Welkow  
 1874: 17 Welkow

- 1878: 5 Godeffroy  
 1879: 8 Drechsel  
 1895: 13 Werner

Compounds with phosphorus compounds.

- 1892: 15 Fink

Bromids.

- 1828: 10 Bonsdorff  
 1894: 9 Smith and Wallace

"Acebrompalladium."

- 1861: 13 Nicklès

Iodids.

- 1825: 8 Pleischl  
 1833: 16 Lassaigue  
 1835: 17 Lassaigue  
 1856: 12 Deville  
 1875: 22 Zenger

IRIDIUM CHLORIDS.

- 1811: 6 ———  
 1814: 4 Vauquelin  
 1834: 16 Kastner  
 1836: 3 Hermann  
 1847: 7 Claus  
 1847: 8 Claus  
 1847: 10 Claus  
 1849: 4 Jewreinow  
 1852: 6 Karmrodt and Uhrlaub  
 1856: 13 Keferstein (cryst.)  
 1858: 7 Claus  
 1860: 6 Gibbs  
 1860: 7 Boedeker  
 1866: 18 Dragendorff  
 1875: 14 Lasaulx (cryst.)  
 1885: 6 Vincent  
 1890: 12 Geisenheimer (with  $\text{PCl}_3$ )  
 1890: 13 Geisenheimer (with  $\text{AsCl}_3$ )  
 1890: 20 Joly  
 1890: 37 Dufet (cryst.)  
 1891: 27 Gladstone  
 1893: 14 Antony  
 1895: 13 Werner

with ethylene.

- 1871: 7 Sadtler

Bromids.

- 1865: 6 Birnbaum  
 1890: 14 Geisenheimer (with  $\text{PBr}_3$ )

Iodids.

- 1835: 17 Lassaigue  
 1857: 7 Oppler

RHODIUM CHLORIDS.

- 1815: 1 Vauquelin  
 1838: 4 Biewend  
 1856: 13 Keferstein (cryst.)  
 1875: 14 Lasaulx (cryst.)  
 1883: 5 Wilm  
 1884: 2 Wilm  
 1885: 7 Vincent  
 1886: 12 Fousereau  
 1888: 10 Leidié  
 1888: 11 Leidié  
 1892: 11 Wilm  
 1895: 13 Werner

OSMIUM CHLORIDS.

- 1836: 3 Hermann

NITROSO CHLORIDS.

- 1896: 9 Brizard

RUTHENIUM CHLORIDS.

- 1847: 10 Claus  
 1857: 12 Senarmont (cryst.)  
 1859: 8 Claus  
 1866: 18 Dragendorff  
 1892: 33 Joly

Nitrosochlorids.

- 1888: 14 Joly  
 1889: 9 Joly  
 1890: 36 Dufet (cryst.)  
 1894: 11 Howe  
 1894: 11 Clark (cryst.)  
 1895: 7 Brizard  
 1896: 8 Brizard

18. COMPOUNDS of platinum with CARBON.

- 1881: 12 Schützenberger  
 1881: 14a Colson  
 1885: 10 Griffiths  
 1890: 15 Schützenberger (and sulfur)  
 1896: 11 Moissan (rhodium, palladium and iridium)  
 1896: 14 Ferreira da Silva (with carbon monoxid)

19. with SILICON.

- 1821: 4 Boussingault  
 1823: 4 Berzelius (also rhodium)  
 1857: 15 Deville  
 1864: 4 Winckler  
 1874: 35 Reichardt  
 1876: 14 Guyard  
 1876: 15 Boussingault  
 1882: 35 Colson

- 1882: 36 Schützenberger and Colson  
 1885: 11 Memminger  
 1886: 4 Miles  
 1893: 30 Warren  
 1896: 12 Vigouroux
20. with TIN.  
 1882: 7 Ditte
21. with PHOSPHORUS.  
 1792: 2 Pelletier  
 1812: 2 Davy  
 1849: 5 Schrötter (also palladium)  
 1883: 10 Clarke and Joslin (with platinum metals)  
 1896: 13 A. Granger
- with arsenic  
 1827: 12 Fischer  
 1884: 4 Tivoli  
 1895: 8 Roessler (also with antimony and bismuth, and with palladium)
- with boron.  
 1859: 17 Martius
22. BROMATES.  
 1841: 9 Rammelsberg (platinum and palladium)
- Iodates.  
 1831: 6 Connell (platinum)  
 1845: 10 Aquilina (platinum)
23. SULFITES.  
 Platinum.  
 1838: 5 Döbereiner  
 1842: 9 Litton and Schnedermann  
 1843: 9 Berthier  
 1847: 7 Claus  
 1861: 9 Lang  
 1866: 7 Birnbaum  
 1869: 12 Birnbaum  
 1890: 10 Seubert and Kobbé
- Palladium.  
 1874: 20 Wöhler
- Iridium.  
 1847: 7 Claus  
 1865: 7 Birnbaum  
 1878: 10 Seubert  
 1890: 10 Seubert and Kobbé
- Osmium and ruthenium.  
 1847: 7 Claus
- Sulfates, iridium.  
 1883: 8 de Boisbaudran  
 1883: 9 de Boisbaudran
- Thiosulfates, platinum.  
 1842: 11 Himly  
 1866: 8 Schottländer  
 1885: 8 Johnson
- Selenates, platinum.  
 1827: 12a Mitscherlich
- Chromates.  
 1892: 6 Frenkel
24. NITRITES.  
 Platinum.  
 1848: 5 Fischer  
 1861: 9 Lang  
 1869: 18 Blomstrand  
 1876: 13 Nilson  
 1877: 7 Thomsen  
 1877: 16 Nilson  
 1877: 17 Nilson  
 1878: 13 Nilson and Pettersson  
 1878: 14 Nilson  
 1879: 12 Groth and Nilson  
 1879: 30 Tropsöe (cryst.)  
 1891: 6 Vèzes  
 1892: 12 Vèzes  
 1893: 18 Vèzes  
 1893: 19 Vèzes
- Palladium.  
 1892: 13 Vèzes
- Iridium.  
 1871: 8 Gibbs  
 1895: 12 Joly and Leidié
- Rhodium.  
 1890: 17 Leidié  
 1890: 18 Wilm
- Ruthenium.  
 1889: 12 Joly and Vèzes  
 1894: 13 Joly and Vèzes
- Phosphates, platinum.  
 1830: 9 Fischer (platinum metals)  
 1866: 10 Gladstone (pyro-phosphotriamate)  
 1880: 6 Engel (hypophosphite)  
 1895: 9 Barnett  
 1896: 16 Finck (phospho-palladic ethers)

- Arsenates.  
   1820: 2 Thomson (platinum, palladium and rhodium)  
   1886: 5 Gibbs (platinum)  
 Arsenites.  
   1894: 12 Reichard (platinum and palladium)  
   1895: 10 Stavenhagen  
 "Cobaltate," platinum.  
   1799: 4 Brugnatelli  
   1896: 34 Hazen  
 Stannates, platinum.  
   1884: 3 Schützenberger  
 Thiostannates, platinum.  
   1892: 14 Schneider  
 Selenostannates, platinum.  
   1891: 9 Schneider  
 Platomolybdates.  
   1790: 2 Hielm  
   1877: 15 Gibbs  
   1886: 5 Gibbs  
   1895: 11 Gibbs  
 Platotungstates.  
   1877: 15 Gibbs  
   1886: 5 Gibbs  
   1891: 8 Rosenheim  
   1895: 11 Gibbs  
 25. CYANIDS.  
   1860: 14 Martius  
   1893: 22 Werner  
 Platinum.  
   1822: 2 Gmelin and Wöhler  
   1836: 4 Döbereiner  
   1837: 7 Rammelsberg  
   1842: 8 Kane  
   1842: 10 Knop  
   1842: 16 Haidlen and Fresenius  
   1847: 14 Quadrat  
   1847: 15 Rammelsberg  
   1847: 16 Laurent  
   1847: 17 Haidinger (opt.)  
   1847: 18 Haidinger (opt.)  
   1848: 9 Baumert  
   1849: 7 Haidinger (opt.)  
   1850: 9 Schabus  
   1850: 16 Brewster (opt.)  
   1852: 10 Haidinger (opt.)  
   1853: 9 Stokes (opt.)  
   1853: 10 Stokes (opt.)  
   1855: 12 Schafarik  
   1855: 13 Böttger (opt.)  
   1855: 14 Stokes (opt.)  
   1855: 20 Haidinger (opt.)  
   1856: 7 Weselsky  
   1857: 8 Schwarzenbach  
   1857: 13 Grailich and Lang (cryst.)  
   1857: 14 Descloizeaux (cryst.)  
   1858: 17 Grailich (opt.)  
   1859: 12 Knop  
   1859: 13 Werther  
   1859: 14 Schwarzenbach  
   1859: 18 Becquerel (opt.)  
   1859: 19 Greiss (opt.)  
   1860: 12 Hadow  
   1860: 13 Czudnowicz  
   1860: 16 von Rath (opt.)  
   1861: 12 Lange  
   1863: 6 Debus  
   1863: 7 Dellfs  
   1863: 18 Quinke (opt.)  
   1864: 11 Ditscheiner (cryst.)  
   1865: 9 van der Burg  
   1866: 11 Rössler  
   1866: 28 Lang  
   1867: 8 Carstanjen  
   1868: 3 Diakonow  
   1869: 15 Weselsky  
   1869: 17 Blomstrand  
   1869: 18 Blomstrand  
   1870: 19 Preiss  
   1870: 29 Schoras (opt.)  
   1871: 9 Friswell  
   1871: 10 Toczynski  
   1872: 6 Cleve and Hoeglund (cryst.)  
   1872: 7 Bolton  
   1873: 11 Holst  
   1874: 18 Cleve  
   1874: 24 Jolin  
   1874: 31 Topsöe (cryst.)  
   1874: 40 Hagenbach-Bischoff (opt.)  
   1875: 19 Atterberg  
   1875: 20 Vidau  
   1877: 18 Friswell and Greenaway  
   1878: 17 Bertin  
   1879: 31 Lommel (cryst.)  
   1880: 11 Scholtz  
   1880: 12 Richard and Bertrand  
   1880: 30 Wiedemann (opt.)  
   1880: 31 Lommel (opt.)  
   1880: 32 Lommel (opt.)  
   1881: 30 Lommel (opt.)  
   1883: 12 Cleve

- 1883: 19 König (opt.)  
 1885: 3 Cleve  
 1886: 6 Wilm  
 1886: 7 Wilm  
 1886: 13 Lehmann  
 1887: 9 Wilm  
 1887: 39 Himly, Leiser and Bard-  
           thold  
 1888: 16 Wilm  
 1888: 17 Freund  
 1888: 25 Walden  
 1888: 26 Rüdorff  
 1889: 13 Wilm  
 1893: 26 Wilm  
 1895: 13 Werner  
 1895: 41 Macintyre  
 1896: 21 Schertel  
 1896: 41 Jackson

## Palladium.

- 1822: 2 Gmelin and Wöhler  
 1837: 7 Rammelsberg  
 1852: 10 Haidinger (opt.)  
 1853: 2 Béchamp  
 1856: 13 Keferstein (cryst.)  
 1866: 11 Rössler  
 1869: 15 Weselsky

## Iridium.

- 1834: 12a Booth  
 1837: 7 Rammelsberg  
 1852: 10 Haidinger (opt.)

## Osmium.

- 1895: 31 Dufet (cryst.)

## Ruthenium.

- 1895: 31 Dufet (cryst.)  
 1896: 22 Howe

## Osmiamic acid.

- 1846: 10 Fritsche and Struve  
 1891: 15 Joly

## 26. THIOCYANATES.

## Platinum.

- 1854: 9 Buckton  
 1856: 5 Claus  
 1856: 13 Keferstein  
 1868: 4 Skey  
 1868: 5 Marciano  
 1869: 14 Schneider  
 1869: 18 Blomstrand  
 1874: 21 Skey  
 1874: 22 Skey  
 1877: 19 Wyruboff  
 1877: 42 Clarke  
 1880: 9 Wyruboff

- 1880: 10 Marciano  
 1881: 13 Clarke and Owens  
 1891: 7 Guareschi

## Palladium.

- 1867: 7 Croft  
 1875: 16 Kern

## Selenocyanates, platinum.

- 1878: 18 Clarke

## 27. BASES.

## AMMONIUM.

- 1856: 6 Claus  
 1856: 8 Weltzien  
 1862: 12 Schiff  
 1893: 22 Werner  
 1895: 13 Werner

## Platinum.

- 1828: 11 Magnus  
 1837: 6 Simon  
 1838: 6 Gros  
 1838: 7 Kane  
 1840: 5 Reiset  
 1841: 10 Berzelius  
 1841: 11 Kane  
 1844: 11 Peyrone  
 1844: 12 Reiset  
 1844: 13 Blyth  
 1846: 5 Knop and Schneder-  
           mann  
 1846: 6 Haidinger (opt.)  
 1846: 11 Raewsky  
 1847: 12 Claus  
 1847: 13 Peyrone  
 1849: 6 Laurent and Gerhardt  
 1850: 8 Gerhardt  
 1851: 7 Hofmann  
 1851: 8 Buckton  
 1852: 8 Buckton  
 1854: 7 Claus  
 1855: 10 Peyrone  
 1855: 11 Peyrone  
 1856: 9 Grimm  
 1856: 10 Grimm  
 1857: 11 Sella (cryst.)  
 1860: 15 Church and Owens  
 1864: 3 Gentile  
 1865: 4 Cleve  
 1866: 12 Cleve  
 1866: 13 Hadow  
 1867: 9 Cleve  
 1867: 10 Thomsen  
 1869: 16 Thomsen  
 1869: 17 Blomstrand



1870: 11 Cleve  
 1870: 12 Cleve  
 1870: 13 Gordon  
 1870: 14 Blomstrand  
 1870: 15 Phillips  
 1870: 16 Odling  
 1871: 12 Cleve  
 1871: 13 Cleve  
 1871: 14 Cleve  
 1871: 15 Cleve  
 1871: 16 Blomstrand  
 1871: 17 Blomstrand  
 1872: 9 Topsøe (cryst.)  
 1873: 10 Sharples  
 1876: 30 Thomsen (thermo-  
       chem.)  
 1878: 15 Phillips  
 1879: 15 Drechsel  
 1882: 8 Gerdes  
 1882: 9 Drechsel  
 1882: 20 Hofmeister  
 1883: 20 Blomstrand  
 1884: 15 Drechsel  
 1886: 8 Jörgensen  
 1887: 10 Cossa  
 1887: 11 Reese  
 1888: 19 Karfoed  
 1888: 20 Haberland and Hane-  
       kop  
 1889: 15 Jörgensen  
 1890: 21 Jörgensen  
 1890: 22 Jörgensen  
 1890: 23 Jörgensen  
 1890: 24 Cossa  
 1890: 25 Carlgren  
 1890: 26 Carlgren and Cleve  
 1892: 16 Petersen  
 1893: 23 Werner and Miolati  
 1894: 15 Cossa  
 1894: 17 Werner and Miolati  
 1894: 26 Kurnakow  
 1895: 13 Werner  
 1895: 14 Kurnakow  
 1895: 17 Klason  
 1895: 18 Klason  
 1896: 17 Schou  
 1896: 20 Werner.

#### Palladium.

1841: 12 Fehling  
 1853: 1 Müller  
 1860: 6 Gibbs  
 1865: 5 Baubigny  
 1878: 16 Deville and Debray  
 1880: 7 Isambert  
 1890: 39 Smith and Keller

#### Iridium.

1852: 7 Skoblikoff  
 1879: 11 Birnbaum  
 1889: 14 Palmaer  
 1895: 16 Palmaer  
 1895: 16a Palmaer  
 1896: 18 Palmaer

#### Rhodium.

1882: 11 Jörgensen  
 1883: 13 Jörgensen  
 1884: 6 Jörgensen  
 1886: 9 Jörgensen  
 1889: 15 Jörgensen  
 1890: 23 Jörgensen  
 1891: 19 Jörgensen  
 1891: 20 Jörgensen  
 1892: 18 Jörgensen  
 1892: 19 Jörgensen  
 1893: 20 Jörgensen  
 1894: 16 Jörgensen  
 1896: 19 Jörgensen

#### Osmium.

1858: 5 Gibbs and Genth  
 1860: 6 Gibbs  
 1881: 7 Gibbs

#### Ruthenium.

1889: 11 Joly  
 1890: 19 Joly  
 1892: 20 Joly  
 1893: 34 Mangin  
 1893: 35 Nicolle and Cantacu-  
       zène  
 1895: 15 Witt and Buntrock

#### Platinum bases with HYDROXYL- AMIN.

1871: 11 Lossen  
 1887: 12 Alexander

#### with ETHYLAMIN.

1892: 21 Cossa

#### with ANILIN.

1848: 7 Raewsky  
 1870: 12 Cleve

#### with PYRIDIN.

1885: 14 Hedin  
 1892: 21 Cossa  
 1893: 21 Cossa  
 1895: 18 Klason  
 1896: 20 Werner

#### with PYRAZOL.

1891: 18 Balbiano  
 1892: 22 Balbiano

with NICOTIN.

1848: 6 Raewsky

with CONHN.

1848: 8 Blyth

with ACETONAMIN.

1876: 17 Heintz

#### PLATINUM-SULFUR BASES.

1876: 16 Krüger

1885: 12 Enebuske

1885: 13 Rudelius

1887: 7 Löhndahl

1888: 15 Blomstrand

1890: 16 Löhndahl

1895: 19 Klason

1895: 19a Hamberg

#### Mercaptids.

1834: 12 Zeise (platinum)

1844: 10 Wertheim (platinum)

1877: 13 Claesson (platinum, iridium and rhodium)

#### Cacodyl compounds.

1842: 12 Bunsen

### 28. ORGANIC COMPOUNDS.

#### Platinum ethyl.

1852: 11 Knop

#### Oxalates, platinum.

1833: 15 Döbereiner

1847: 17 Haidinger (opt.)

1847: 18 Haidinger (opt.)

1858: 6 Souchay and Lennsen

1859: 16 Schlossberger

1885: 15 Söderbaum

1888: 18 Söderbaum

1894: 14 Söderbaum

1896: 20 Werner

#### Rhodium.

1890: 36 Dufet (cryst.)

#### Ureas, platinum.

1881: 13 Clarke and Owens

#### Thionreas, platinum.

1893: 24 Kurnakow

1893: 25 Sell and Easterfield

#### Fulminates, platinum.

1817: 5 Davy

1829: 11 Davy

1878: 12 von Meyer

#### Platinum compounds with soap.

1790: 3 Leonhardi

with anthrazothionhydrate.

1817: 6 Grotthus

with camphoric acid.

1823: 5 Brandes

with œnanthic acid.

1837: 9 Mulder

with thiolactic acid.

1883: 11 Lovin

with glyecocol.

1892: 23 Wallin

### 29. CONDENSATION OF HYDROGEN ON PLATINUM (see also Condensation phenomena, 47).

1823: 7 Döbereiner

1823: 8 Döbereiner

1833: 22 Boussingault

1836: 4 Döbereiner

1868: 10 Graham

1873: 3 Dewar

1873: 21 Merget

1873: 22 Pellet

1874: 9 Favre

1874: 10 Favre

1875: 10 Smith

1880: 18 Phipson

1880: 19 Tommasi

1885: 22 Kritscherosky

1892: 68 Krakau

1896: 23 Friedländer (argon)

#### Palladium.

1868: 10 Graham

1869: 4 Graham

1869: 5 Graham

1869: 6 Wurtz

1869: 7 Böttger

1869: 8 Roberts

1869: 9 Dewar

1869: 10 Hofmann

1870: 2 Favre

1871: 2 Böttger

1871: 3 Lisenko

1871: 4 Mohr

1871: 5 Kolbe

1872: 2 Roberts and Wright

1872: 17 Saytzeff

1874: 7 Troost and Hautefeuille

1874: 8 Moutier

1874: 9 Favre

1874: 10 Favre

1874: 12 Smith

1874: 38 Böttger

1875: 10 Smith

- 1875: 11 Laudy  
 1876: 56 Böttger  
 1883: 4 De la Rue and Müller  
 1884: 29 Knott  
 1885: 17 Schiff  
 1885: 37 Larroque  
 1885: 39 Traube  
 1886: 34 Knott  
 1887: 21 Keiser  
 1895: 4 Hoitsema  
 1895: 5 Krakau  
 1895: 35 Mond, Ramsay, and  
     Shields  
 1896: 24 Tilden (helium)

## 30. ANALYSIS. REACTIONS.

- 1828: 13 Fischer  
 1862: 10 Claus  
 1866: 19 Bunsen (flame)  
 1871: 20 Jean ( $\text{Na}_2\text{S}$ )  
 1891: 34 Behrens (microchem-  
     ical)  
 1894: 22 Phillips (H)

## Platinum.

- 1826: 8 Forchhammer ( $\text{HgNO}_3$ )  
 1824: 1 Le Baillif (I and  $\text{CuCl}$ )  
 1832: 6 Lassaigne (I)  
 1836: 6 Buchner  
 1845: 11 Cottureau (I)  
 1855: 15 Vohl ( $\text{Na}_2\text{S}_2\text{O}_3$ )  
 1858: 9 Spiller (citric acid)  
 1867: 13 von Schwarzenbach  
     (albumen)  
 1876: 24 Kern (Mg)  
 1877: 22 Heintz (C)  
 1877: 23 Jörgensen ( $\text{AgNO}_3$ )  
 1878: 21 Böttger (P)  
 1880: 15 Ditte ( $\text{HCl}$ )  
 1880: 22 Vincent (dimethyl-  
     amin)  
 1881: 19 Field  
 1883: 25 Orłowski ( $((\text{NH}_4)_2\text{S}_2\text{O}_3)$ )

## Palladium.

- 1824: 1 Le Baillif (I and  $\text{CuCl}$ )  
 1828: 15 Wetzlar ( $\text{CuCl}$ )  
 1838: 11 Lassaigne (I)  
 1851: 9 Lassaigne (I)  
 1875: 17 Kern (I and  
      $\text{K}_4\text{Fe}(\text{CN})_6$ )  
 1876: 24 Kern (Mg)  
 1876: 25 Kern (I and  
      $\text{K}_4\text{Fe}(\text{CN})_6$ )  
 1880: 24 von Fodor ( $\text{CO}$ )  
 1880: 21 Vincent (dimethyla-  
     min)

## Iridium.

- 1883: 7 de Boisbaudran

## Rhodium.

- 1844: 6 Claus ( $\text{CaO}$ )  
 1844: 6 Claus (boric acid)  
 1885: 18 Demarçay ( $\text{NaOCl}$ )

## Ruthenium.

- 1846: 8 Claus  
 1867: 12 Lea ( $\text{Na}_2\text{S}_2\text{O}_3$ )  
 1894: 11 Howe

## Impurities.

- 1877: 26 Galwalovski  
 1879: 23 Gintl  
 1890: 30 Classen

## 31. ESTIMATION.

- 1879: 34 Deville and Mascart  
 1891: 31 Joly and Leidié

## Platinum.

- 1835: 9 Döbereiner  
 1869: 19 Scheibler  
 1870: 17 Topsøe  
 1870: 19 Preiss (cyanids)  
 1877: 10 Ribau  
 1881: 24 Wallach (organic com-  
     pounds)  
 1885: 30 Oudemans (also iri-  
     dium and ruthenium)  
 1894: 28 Gulewitsch  
 1895: 22 de Koninck

## Palladium.

- 1875: 22 Zenger  
 1892: 6 Frenkel  
 1878: 23 Volhard (effect of pal-  
     ladium on estimation  
     of silver)

## 32. By ASSAY.

- 1879: 24 Perry  
 1880: 29 van Riemsdijk  
 1882: 26 van Riemsdijk  
 1892: 42 Matthey  
 1895: 21 Priwosnik (influence  
     on gold assay)

## Platinum.

- 1816: 2 Chaudet  
 1837: 10 Haindl  
 1878: 19 von Jüptner  
 1881: 29 Balling  
 1885: 21 van Riemsdijk  
 1890: 42 Matthey

## Iridium and osmium.

- 1834: 17 Berthier  
1857: 6 Wysocky (gold in presence of osmiridium)

## By ELECTROLYSIS.

- 1892: 40 Smith

## Platinum.

- 1880: 26 Luckow  
1884: 14 Classen  
1891: 28 Smith  
1891: 29 Smith and Muhr  
1892: 40 Rüdorff

## Palladium.

- 1880: 27 Schucht  
1890: 40 Smith and Keller  
1890: 41 Smith and Frankel  
1891: 28 Smith  
1891: 29 Smith and Muhr

## Rhodium.

- 1891: 30 Joly and Leidié  
1891: 32 Smith

## Ruthenium.

- 1895: 20 Smith and Harris

## 33. SEPARATIONS.

## Platinum and palladium.

- 1896: 26 Cohn and Fleissner

## Iridium and platinum.

- 1855: 4 Saint-Gilles  
1892: 37 Antony

## Platinum metals.

- 1878: 24 de Clermont and Frommel (from As)  
1880: 25 von Jüptner (Cd)  
1883: 27 de Boisbaudran (Ga)  
1887: 25 Krüss and Hoffman (Au)  
1887: 26 Bettel (Au)  
1887: 27 Pirngruber (Au)  
1887: 28 Wyatt (Au)

## Platinum.

- 1829: 16 Lampadius (Ag)  
1875: 6 ——— (Ag)  
1841: 13 Kemp (Au)  
1845: 13 Elsner (Sn, As)  
1861: 16 Béchamp and Saint-Pierre (Sn, Sb)  
1879: 28 de Clermont (As, Sn, Sb)  
1881: 18 Campari (As, Sn, Sb)  
1886: 14 Fresenius (As, Sn, Sb)

- 1886: 15 Dirvell (As, Sn, Sb)  
1886: 16 Bailey (As, Sn, Sb)  
1888: 33 de Koninck and Lecremier (As, Sn, Sb)  
1892: 38 Antony and Nicolli (As, Sn, Sb)  
1876: 22 Becker (Te)  
1882: 22 de Boisbaudran (Ga)  
1887: 23 Warren (Ti)  
1843: 9 Berthier (by SO<sub>2</sub>)

## Palladium.

- 1875: 6 ——— (Ag)  
1887: 24 Rosenblatt (Hg)  
1866: 15 Wöhler (Cu)  
1887: 24 Rosenblatt (Pb, Bi, Cu)  
1882: 22 de Boisbaudran (Ga)

## Iridium.

- 1829: 17 Lampadius

## 34. ANALYTICAL USES.

## Platinum tetrachlorid for analysis of alkalies.

- 1799: 3 Vauquelin  
1821: 6 Pfaff  
1832: 6 Lassaigue  
1846: 13 Fresenius  
1865: 8 Redtenbacher  
1866: 17 Finkener  
1868: 11 Chalmers and Tatlock  
1874: 26 Krause  
1876: 23 Kretschy  
1877: 25 Fresenius  
1879: 22 Precht  
1880: 23 Morrell  
1881: 20 Lindo  
1881: 21 Ulex  
1881: 22 Tatlock  
1881: 23 Zuchschwerdt and West  
1882: 23 Fresenius  
1883: 23 Stolba  
1885: 20 Böttger and Precht  
1887: 13 Dittmar and McArthur  
1888: 37 de Koninck  
1892: 45 Jean and Trillat  
1893: 38 Villiers and Borg  
1895: 23 Winter  
1895: 24 van Dam  
1895: 25 Delépine  
1895: 27 Sonstadt  
1896: 28 Hintz  
1896: 29 Fabre  
1896: 31 Ruer  
1896: 32 Bauer  
1896: 33 Precht

- 1828: 28 Dublanc (for I)  
 1829: 23 Wöhler (combustion of C)  
 1831: 21 Hare (platinized asbestos)  
 1834: 15 Brandes (for tartaric acid)  
 1855: 22 Stenhouse (platinized charcoal)  
 1863: 7 Dellfs (cyanid for alkaloids)  
 1876: 31 Kopfer (elementary analysis)  
 1876: 32 Kopfer (elementary analysis)  
 1876: 33 Mitscherlich (chlorid for oxygen)  
 1878: 29 Kopfer (elementary analysis)  
 1881: 19 Field (iodid in water analysis)  
 1882: 25 Blunt (indicator for I)  
 1883: 24 Leeds (iodid for water analysis)  
 1883: 26 Ballo (platinized magnesium)  
 1883: 28 Clemence (platinum tube)  
 1884: 13 Zulkowsky and Lepéz (platinized quartz)  
 1888: 28 Barfoed (for Hg)  
 1888: 35 Kassner (for ash analysis)  
 1890: 38 Thiele (PtZn in Marsh's test)  
 1896: 27 Tarugi (amalgam)  
 1896: 34 Hazen (cobaltite for colometric standard)

#### Palladium.

- 1857: 10 Böttger (for gases)  
 1879: 25 Hempel (use in analysis of CO<sub>2</sub>)  
 1881: 27 Schneider (use in analysis of CO<sub>2</sub>)  
 1889: 20 Winkler (use in analysis of CO<sub>2</sub>)  
 1884: 18 Vulpinus (for O<sub>2</sub>)  
 1882: 25 Maggi (chlorid in water analysis)  
 1853: 3 Kersting (iodid)  
 1876: 21 Chatin (iodid)  
 1884: 17 Harnack (iodid)  
 1875: 21 Selmi (iodid for alkaloids)  
 1879: 26 Hempel (metal for hydrogen)

- 1879: 27 Hempel (do.)  
 1881: 26 Tschirikoff (do.)  
 1886: 18 Hoppe-Seyler (do.)  
 1886: 19 Sudakoff (do.)  
 1885: 22 Kritschewsky (do.)  
 1895: 30 Phillips (chlorid for hydrogen)  
 1896: 30 Campbell and Hart (do.)  
 1895: 34 Campbell (palladinized CuO in organic analysis)

#### Ruthenium.

- 1862: 9 Claus  
 1866: 18 Dragendorff (chlorid and iridium chlorid for alkaloids)

### 35. CHEMICAL PROPERTIES—Solubility, etc.

#### Platinum.

- 1751: 2 Scheffer  
 1755: 1 Lewis  
 1761: 1 Marggraf  
 1779: 1 Tillet  
 1782: 2 Wenzel  
 1799: 2 Priestly  
 1810: 4 Davy  
 1811: 3 Davy  
 1827: 14 Fischer  
 1828: 12 Döbereiner  
 1836: 14 Döbereiner  
 1842: 14 Millon  
 1854: 13 How  
 1854: 14 Lasch  
 1859: 10 Dullo  
 1866: 6 Schönbein  
 1875: 25 Fairley  
 1878: 22 Berthelot  
 1879: 14 Edison

#### Palladium.

- 1809: 2 Cloud  
 1811: 3 Davy  
 1827: 14 Fischer  
 1878: 22 Berthelot

#### Action in promoting solution of other metals.

- 1829: 15 Zenneck (platinum)  
 1838: 23 Döbereiner (iridosmium)  
 1854: 12 ——— (iridosmium)  
 1873: 23 Gourdon (platinum)  
 1870: 30 Schönn (passive iron)

## 36. AFFINITY.

- 1883: 21 Donath and Mayrhofer  
1888: 21 Heyes (valence)

## Platinum.

- 1819: 1 Berzelius  
1874: 25 Gramp  
1878: 42 Berthelot  
1881: 10 Orłowsky (toward sulfur)

## Palladium.

- 1804: 20 Ritter  
1874: 25 Gramp  
1878: 42 Berthelot  
1888: 22 Schürmann

## 37. ACTION ON COMPOUNDS—

## Platinum.

- 1817: 4 Gehlen ( $\text{As}_2\text{O}_3$ , etc.)  
1874: 27 Deville and Debray (formic acid)  
1878: 51 Tommasi ( $\text{FeCl}_3$  and  $\text{AgCl}$ )  
1881: 40 Johnston (mixture of N and H)  
1893: 32 Mahon (iron compounds)  
1894: 27 Michaud (ammonium amalgam)

## ACTION ON GASES.

- 1892: 30 Emich (NO)  
1893: 29 Dudley (mixture of HCl and O)

## Platinum.

- 1892: 29 Neumann  
1838: 15 Böttger (Cl)  
1877: 20 Troost and Hautefeuille (Cl)  
1879: 16 Volta (ozone)  
1836: 7 Regnault (steam)  
1846: 22 Grove (steam)  
1847: 26 Wilson (steam)  
1876: 26 Deville and Debray (steam)  
1829: 27 Despretz (ammonia)  
1864: 6 Geitner ( $\text{SO}_2$ )  
1890: 29 Uhl ( $\text{SO}_2$ )  
1896: 35 Mulder ( $\text{SO}_2$ )  
1866: 14 Böttger ( $\text{H}_2\text{S}$ )  
1870: 34 Skey ( $\text{H}_2\text{S}$ )  
1842: 15 Marchand (hydrocarbons)  
1881: 6 Wilm (hydrocarbons)  
1861: 11 Baudrimont ( $\text{PCl}_5$ )  
1864: 2 Baudrimont ( $\text{PCl}_5$ )  
1880: 20 Goldschmidt ( $\text{PCl}_5$ )

- 1885: 9 Moissan ( $\text{PF}_3$ )  
1891: 21 Sudborough (NOCl)  
1892: 31 Sabatier and Senderens ( $\text{NO}_2$ )

## Palladium.

- 1892: 29 Neumann  
1838: 15 Böttger (Cl)  
1879: 16 Volta (ozone)  
1882: 17 Mailfert (ozone)  
1890: 29 Uhl ( $\text{SO}_2$ )  
1842: 15 Marchand (hydrocarbons)  
1881: 6 Wilm (hydrocarbons)  
1892: 31 Sabatier and Senderens ( $\text{NO}_2$ )

## Iridium.

- 1892: 32 Antony (Cl and CO)

## Osmiridium.

- 1846: 22 Grove (steam)

## Rhodium.

- 1881: 6 Wilm (hydrocarbons)

## 38. PHYSIOLOGICAL ACTION.

- 1825: 10 Gmelin

## Platinum.

- 1833: 25 Prevost (chlorid)  
1840: 7 Höfer  
1878: 27 Brunton and Fayer (on cobra poison)  
1878: 28 Pedlar (on cobra poison)  
1882: 20 Hofmeister (bases)  
1892: 36 Pell (chlorid)

## Palladium.

- 1871: 18 Rabuteau (chlorid)

## "Osmic acid."

- 1849: 8 Brauell  
1851: 10 Butlerow  
1874: 28 Deville

## Osmiamic acid.

- 1869: 20 Owsjannikow

## 39. CRYSTALLOGRAPHY.

- 1843: 7 Berzelius

## Platinum, metal.

- 1820: 5 Sowerby  
1830: 3 Marx  
1840: 2 Jacquelin  
1851: 4 Ebelmen  
1855: 2 Mallet  
1857: 4 Köttig

- 1858: 10 Noquès  
 1859: 5 Sorèze  
 1860: 1 Cotta  
 1862: 5 Phipson  
 1862: 6 Noble  
 1879: 6 Deville and Debray  
           (preparation of FePt)

## Palladium.

- 1842: 7 Rose  
 1849: 10 Rose  
 1853: 4 Nicklès  
 1856: 13 Keferstein

## Iridium.

- 1841: 5 Rose  
 1849: 10 Rose  
 1853: 4 Nicklès  
 1866: 3 Cloez  
 1893: 27 Prinz

## Osmium.

- 1894: 10 Rose

## Osmiridium and iridosmium.

- 1828: 6 Breithaupt  
 1830: 3 Marx  
 1833: 10 Breithaupt  
 1833: 11 Breithaupt  
 1840: 1 Breithaupt  
 1882: 1 von Lasaulx

## Ruthenium.

- 1879: 6 Deville and Debray  
           (synthetic laurite)

## HALOGEN SALTS.

## Platinum.

- 1854: 15 Schabus  
 1855: 16 Weltzien  
 1855: 17 Marignac  
 1857: 14 Descloizeaux  
 1861: 2 Sella  
 1868: 8 Topsøe  
 1871: 19 Topsøe and Christian-  
           sen  
 1873: 5 Marignac  
 1874: 31 Topsøe  
 1874: 41 Topsøe  
 1877: 27 Schimper  
 1882: 21 Topsøe  
 1888: 9 Weibull

## Palladium.

- 1869: 11 Topsøe

## Iridium and rhodium.

- 1856: 13 Keferstein  
 1875: 14 Lasaulx  
 1890: 37 Dufet (iridium)

## Ruthenium.

- 1857: 12 Senarmont  
 1890: 36 Dufet  
 1894: 11 Clark

## NITRITES, platinum.

- 1879: 12 Groth and Nilson  
 1879: 30 Topsøe  
 1880: 33 Groth

## BASES, platinum.

- 1857: 11 Sella  
 1895: 32 Sella

## Iridium.

- 1895: 16 Palmaer  
 1895: 16*a* Palmaer  
 1895: 19*a* Hamberg

## CYANIDS, platinum.

- 1857: 13 Grailich and Lang  
 1857: 14 Descloizeaux  
 1864: 11 Ditscheiner  
 1866: 28 Lang  
 1872: 6 Cleve and Hoeglund  
 1874: 31 Topsøe  
 1879: 31 Lommel  
 1880: 11 Scholtz  
 1856: 13 Keferstein (palladium)  
 1895: 31 Dufet (osmium and  
           ruthenium)

## THIOCYANATES.

- 1856: 13 Keferstein  
 1877: 19 Wyruboff

## OXALATES, rhodium.

- 1890: 36 Dufet

## RUTHENATES.

- 1890: 35 Dufet

40. OPTICAL PROPERTIES of  
crystals.

## Halogen compounds.

- 1852: 10 Haidinger (palladium  
           and rhodium)  
 1854: 11 Gladstone (platinum)  
 1871: 19 Topsøe and Christian-  
           sen (platinum)  
 1895: 33 Gladstone and Hibbert  
           (platinum)

## Sulfids.

- 1864: 14 Pisko (platinum)

## Platinum bases.

- 1846: 6 Haidinger

## Cyanids of platinum.

- 1847: 17 Haidinger (also oxa-  
           lates)

- 1848: 18 Haidinger (also oxalates)  
 1849: 7 Haidinger  
 1850: 16 Brewster  
 1852: 10 Haidinger  
 1853: 9 Stokes  
 1853: 10 Stokes  
 1855: 13 Böttger  
 1855: 14 Stokes  
 1855: 20 Haidinger  
 1858: 17 Grailich  
 1859: 18 Becquerel  
 1859: 19 Greiss  
 1860: 16 von Rath  
 1863: 18 Quincke  
 1870: 29 Schoras  
 1874: 40 Hagenbach-Bischoff  
 1880: 30 Wiedemann  
 1880: 31 Lommel  
 1880: 32 Lommel  
 1881: 30 Lommel  
 1883: 19 König

#### 41. PHYSICAL PROPERTIES.— GENERAL.

##### Platinum.

- 1751: 2 Scheffer  
 1755: 1 Lewis  
 1761: 1 Marggraf  
 1775: 1 Morveau  
 1776: 1 Ingenhousz  
 1798: 1 Morveau  
 1800: 7 Rochon  
 1811: 3 Davy  
 1836: 14 Döbereiner  
 1851: 12 Baudrimont  
 1891: 33 Heräus

##### Palladium.

- 1809: 2 Cloud  
 1811: 3 Davy

##### Osmium.

- 1893: 9 Joly and Vèzes

##### Ruthenium.

- 1893: 8 Joly

#### 42. SPECIFIC GRAVITY.

- 1845: 12 Kopp

##### Platinum.

- 1791: 1 Willir and Norvel  
 1830: 11 Osann  
 1844: 14 Marchand  
 1848: 11 Osann  
 1848: 12 Rose

- 1858: 11 Crace-Calvert and Johnson  
 1875: 26 Deville and Debray  
 1883: 22 —

##### Platinum salts.

- 1873: 30 Schröder  
 1877: 42 Clarke  
 1878: 30 Clarke  
 1885: 19 Groshans  
 1888: 23 Gerlach

##### Palladium.

- 1833: 10 Breithaupt

##### Iridium.

- 1875: 26 Deville and Debray

##### Osmiridium.

- 1833: 10 Breithaupt

##### TENACITY.

- 1809: 4 Morveau (platinum)  
 1834: 25 Karmarsch (platinum)  
 1850: 13 Baudrimont (platinum and palladium)

##### ELASTICITY, platinum.

- 1844: 21 Wertheim (and palladium)  
 1852: 13 Kupffer  
 1854: 17 Kupffer  
 1855: 18 Edlund  
 1876: 64 Pisati  
 1877: 48 Gesechus  
 1887: 42 Bosanquet  
 1888: 47 Rehkul

##### EXPANSIBILITY.

- 1869: 27 Fizeau

##### Platinum.

- 1851: 11 Paucker  
 1858: 11 Crace-Calvert and Johnson  
 1861: 20 Crace-Calvert, Johnson and Lowe  
 1866: 27 Matthiessen (and palladium)  
 1889: 41 Le Chatelier (and platinum-iridium)  
 1891: 50 Seliwano

##### CAPILLARITY.

- 1868: 16 Quincke (platinum and palladium)

##### VISCOSITY.

- 1888: 49 Barus



## PASSIVITY.

1863: 10 Heldt

## 43. FUSIBILITY.

1847: 21 Hare

1847: 22 Hare

1847: 23 Hess

## Platinum.

1775: 2 Bergman

1777: 1 Morveau, etc.

1779: 2 Achard (with arsenic)

1784: 1 Crell

1784: 2 von Sickingen

1789: 1 Willis

1790: 6 Ruprecht

1790: 7 Ruprecht

1791: 2 Born

1800: 3 ———

1802: 4 Marum

1803: 15 Tilloch

1804: 19 Amicus

1806: 6 Corréa

1809: 5 Children

1810: 5 ———

1813: 7 Marcet

1815: 2 Children

1817: 8 Clarke

1817: 9 Clarke

1817: 12 Faraday

1818: 9 Cloud

1818: 10 Prechtl

1819: 2 Gilbert

1819: 3 Clarke

1820: 6 Hare

1826: 12 Nasse

1827: 16 Eichfeld

1835: 19 Maugham

1838: 12 Hare

1839: 6 Geiseler

1840: 8 Hare

1842: 17 Hare

1844: 15 Reich

1845: 19 Riess

1849: 13 Despretz

1852: 12 Deville

1856: 15 Deville

1857: 16 Deville

1859: 7 Jacobi

1860: 4 Deville and Debray

1862: 17 Becquerel

1862: 18 Deville and Debray

1862: 20 Aubel

1862: 21 Heraeus

1863: 11 Richter

1863: 12 Aubel

1869: 21 Skey

1870: 21 Deville

1871: 23 Chapman

1872: 10 Violette

1872: 11 Dumas

1875: 7 ———

1876: 34 Dürre

1879: 43 Violle

1882: 13 Siemens and Hunting-  
ton1892: 35 Heycock and Neville  
(with lead)1894: 19 Heycock and Neville  
(with thallium)

1894: 25 Spring

1895: 43 Holborn and Wien

1896: 37 Meyer

1896: 38 Holman, Lawrence and  
Barr

1896: 39 Hartley

## Palladium.

1818: 9 Cloud

1849: 13 Despretz

1862: 17 Becquerel

1879: 43 Violle

1892: 35 Heycock and Neville  
(with lead)

1895: 43 Holborn and Wien

## Iridium.

1810: 5 ———

1837: 5 Bunsen

1842: 17 Hare

1846: 15 Hare

1879: 43 Violle

1881: 15 Holland (with phos-  
phorus)1882: 14 Dudley (with phos-  
phorus)

1882: 15 Warder

1885: 24 Johnson, Matthey and  
Co.

## Rhodium.

1818: 9 Cloud

1846: 15 Hare

## Iridosmium.

1870: 20 [Farmer]

## VOLATILITY.

## Platinum.

1802: 5 Hare

1858: 12 Elsner

1877: 20 Troost and Hautefeuille  
(in chlorin)

1879: 18 Seelheim (in chlorin)

1879: 19 Meyer (in chlorin)

- 1879: 20 Smith (in chlorin)  
 1879: 21 Dunnington (in chlorin)  
 1879: 45 Edison  
 1886: 29 Dessau  
 1888: 31 Berliner  
 1888: 32 Kayser  
 1891: 40 Crookes  
 1891: 41 Mooser  
 1892: 63 Spring  
 1893: 31 Moissan  
 1896: 40 Moissan
- Palladium.  
 1858: 12 Elsner  
 1888: 31 Berliner  
 1891: 40 Crookes
- Iridium.  
 1858: 12 Elsner  
 1879: 45 Edison
44. MALLEABILITY and making malleable; platinum.  
 1800: 4 Knight  
 1800: 5 Mussin-Puschkin  
 1804: 6 Mussin-Puschkin  
 1804: 15 Mussin-Puschkin  
 1804: 16 Mussin-Puschkin  
 1805: 8 Tilloch  
 1813: 2 Leithner  
 1813: 3 Gehlen  
 1813: 4 Schweigger  
 1813: 5 Wollaston (wire)  
 1814: 11 Scholz  
 1829: 20 Wollaston  
 1831: 27 Abich  
 1832: 15 Marshall  
 1832: 16 Marx  
 1836: 17 Liebig  
 1836: 18 Liebig  
 1841: 15 C.  
 1841: 16 Biewend (palladium)  
 1860: 4 Deville and Debray  
 1860: 18 Delarue  
 1862: 22 [Storer]  
 1875: 7 ———  
 1885: 24 Johnson, Matthey and Co. (iridium)
45. WELDING platinum.  
 1863: 13 Grüel  
 1878: 35 ———  
 1880: 14 Spring (in cold)  
 1884: 20 Seaman  
 1886: 23 Lake
46. THEORETICAL RELATIONS of properties.  
 1826: 15 Berzelius  
 1845: 12 Kopp  
 1883: 21 Donath and Mayrhofer
- Platinum.  
 1818: 8 Montizon  
 1827: 8 Osann  
 1846: 17 Playfair and Joule  
 1860: 17 Crossley  
 1867: 11 Jörgensen  
 1873: 13 Petterson  
 1873: 15 Bottone  
 1882: 34 Kalischer  
 1884: 28 Bidwell  
 1888: 48 Roberts-Austen (palladium and rhodium)  
 1892: 28 Sayno
47. CONDENSATION OF GASES on surface and attendant phenomena (see also Condensation of hydrogen, 29)  
 1834: 19 Faraday  
 1858: 15 Phipson  
 1874: 27 Deville and Debray  
 1894: 35 Cailletet and Collardeau  
 1894: 37 Berthelot
- Platinum.  
 1817: 10 Davy  
 1817: 13 Murray  
 1818: 13 Sömmerring  
 1818: 14 Erman  
 1818: 15 Gill  
 1818: 16 Davy  
 1818: 17 ———  
 1819: 8 Gilbert  
 1822: 6 Döbereiner  
 1822: 7 ———  
 1823: 6 Döbereiner  
 1823: 9 Dulong and Thenard  
 1823: 10 Dulong and Thenard  
 1823: 11 Garden  
 1823: 12 Gmelin  
 1823: 13 Gilbert, Chladin and Daniell  
 1823: 14 Herapath  
 1823: 15 Karmarsch  
 1823: 16 Pfaff  
 1823: 17 Pleischl  
 1823: 19 Schweigger  
 1824: 3 Adie  
 1824: 4 Dana  
 1824: 5 Döbereiner

- 1824: 6 Döbereiner  
 1824: 7 Döbereiner  
 1824: 8 Fyfe  
 1824: 9 Gilbert  
 1824: 10 Henry  
 1824: 11 Kastner  
 1824: 12 Osann  
 1824: 13 Schmidt  
 1824: 14 Turner  
 1824: 15 ———  
 1825: 11 Gill  
 1825: 12 Bischof  
 1825: 13 Davy  
 1825: 14 Vogel  
 1825: 15 John  
 1825: 16 Dulk  
 1825: 17 ———  
 1825: 18 Stratingh  
 1826: 10 Döbereiner  
 1826: 13 Döbereiner  
 1826: 14 Miller  
 1828: 18 Erdmann  
 1829: 22 Liebig  
 1829: 25 Graham  
 1829: 24 Döbereiner  
 1831: 7 Becquerel  
 1831: 9 Döbereiner  
 1831: 10 Schweigger-Seidel  
 1831: 11 Schweigger-Seidel  
 1831: 12 Döbereiner  
 1831: 13 Döbereiner  
 1831: 16 Döbereiner  
 1831: 18 Böttger  
 1831: 19 Schweigger  
 1831: 20 Hess  
 1831: 22 Merryweather  
 1831: 23 Hermbstädt  
 1832: 9 Döbereiner  
 1832: 10 Döbereiner  
 1832: 12 ———  
 1832: 13 Phillips  
 1832: 14 ———  
 1833: 23 Böttger  
 1833: 24 Degen  
 1834: 20 Döbereiner  
 1834: 21 Döbereiner  
 1834: 22 Döbereiner  
 1834: 23 Döbereiner  
 1835: 21 Liebig  
 1835: 22 Artus  
 1835: 23 Hänle  
 1835: 24 Henry  
 1836: 10 Henry  
 1836: 11 Mohr  
 1836: 12 Degen  
 1836: 13 Degen  
 1838: 17 Kuhlmann  
 1838: 18 Kuhlmann  
 1839: 7 Kuhlmann  
 1839: 8 Martens  
 1839: 9 Grove  
 1839: 10 Grove  
 1839: 12 Schönbein  
 1843: 10 Böttger  
 1843: 11 Döbereiner  
 1843: 12 Döbereiner  
 1843: 13 Reiset and Millon  
 1843: 14 Schönbein  
 1844: 17 Döbereiner  
 1844: 20 Döbereiner  
 1845: 16 Döbereiner  
 1845: 17 Schönbein  
 1845: 18 Schrötter  
 1849: 12 Field  
 1850: 15 Wagner  
 1853: 11 Magnus  
 1855: 23 Baudrimont  
 1857: 20 Schönbein  
 1858: 16 Schönbein  
 1859: 26 Schönbein  
 1859: 27 Schönbein  
 1861: 19 Saint-Edme  
 1861: 21 Gorup-Besanez  
 1862: 25 Wiederholt  
 1865: 17 Kraut  
 1865: 18 Sell  
 1866: 14 Böttger  
 1866: 26 Wilde  
 1867: 19 Merz  
 1867: 20 Artus  
 1868: 10 Graham  
 1870: 35 Skey  
 1871: 25 Klinkerfues  
 1871: 26 Baudrimont  
 1873: 24 Grüel  
 1873: 27 Coquillion  
 1873: 29 Favre  
 1874: 11 Smith  
 1874: 37 Wilde  
 1874: 38 Traube  
 1875: 10 Smith  
 1875: 25 Fairley  
 1875: 32 Coquillion  
 1876: 27 Wöhler  
 1876: 57 Meyer  
 1876: 58 Meyer  
 1876: 59 Dumas  
 1878: 46 Coquillion  
 1878: 52 Hoppe-Seyler  
 1878: 53 Gladstone and Tribe  
 1879: 49 Gladstone and Tribe  
 1879: 51 Koch  
 1882: 39 Berthelot  
 1882: 42 Traube

1883: 32 Chappuis  
 1883: 34 Fromme  
 1884: 12 Valentini  
 1884: 13 Zulkowsky and Lepéz  
 1885: 44 Bellamy  
 1886: 27 Grimaux  
 1886: 28 Ihmori  
 1886: 32 Warburg and Ihmori  
 1887: 20 Cooke  
 1887: 40 Kraut  
 1887: 41 Ihmori  
 1887: 54 Wright and Thompson  
 1888: 29 Hodgkinson and Lowndes  
 1888: 30 Berliner  
 1889: 21 Jahn  
 1889: 24 Traube  
 1889: 27 Ilosvay de N. Ilosva  
 1889: 29 Fuchs  
 1890: 31 Engel  
 1890: 33 Loew  
 1890: 34 Loew  
 1890: 59 Elster and Geitel  
 1891: 24 Neumann and Streintz  
 1891: 38 Warren  
 1892: 10 Wilm  
 1895: 35 Mond, Ramsay and Shields

#### Palladium.

1817: 10 Davy  
 1817: 11 Schübler  
 1823: 9 Dulong and Thenard  
 1823: 18 Pleischl  
 1825: 19 Wöhler  
 1826: 9 Miller  
 1868: 10 Graham  
 1869: 4 Graham  
 1869: 5 Graham  
 1869: 6 Wurtz  
 1869: 7 Böttger  
 1869: 8 Roberts  
 1869: 9 Dewar  
 1869: 10 Hofmann  
 1869: 30 Böttger  
 1873: 25 Böttger  
 1873: 26 Böttger  
 1873: 27 Coquillion  
 1875: 10 Smith  
 1875: 12 Troost and Hautefeuille  
 1875: 32 Coquillion  
 1876: 53 Coquillion  
 1876: 54 Coquillion  
 1877: 39 Tommasi  
 1877: 40 Coquillion  
 1877: 41 Coquillion

1878: 46 Coquillion  
 1878: 52 Hoppe-Seyler  
 1878: 53 Gladstone and Tribe  
 1879: 27 Hempel  
 1879: 49 Gladstone and Tribe  
 1879: 50 Hoppe-Seyler  
 1879: 51 Koch  
 1881: 26 Tschirikoff  
 1881: 36 Baumann  
 1881: 40 Traube  
 1882: 41 Traube  
 1882: 42 Traube  
 1883: 30 Traube  
 1883: 31 Hoppe-Seyler  
 1883: 34 Fromme  
 1883: 39 Baumann  
 1887: 40 Kraut  
 1888: 30 Berliner  
 1889: 24 Traube  
 1889: 25 Hoppe-Seyler  
 1889: 26 Thoma  
 1891: 24 Neumann and Streintz  
 1894: 21 Phillips  
 1895: 35 Mond, Ramsay and Shields

#### Iridium.

1823: 9 Dulong and Thenard  
 1823: 11 Garden  
 1831: 14 Döbereiner  
 1831: 15 Döbereiner  
 1831: 16 Döbereiner  
 1883: 31 Hoppe-Seyler

#### Rhodium.

1881: 5 Wilm  
 1883: 31 Hoppe-Seyler

#### 48. DIFFUSION OF GASES through platinum.

1863: 8 Matteucci  
 1863: 9 Deville and Debray  
 1866: 25 Graham  
 1876: 61 Helmholtz and Root

#### Palladium.

1894: 34 Ramsay  
 1895: 34 Campbell

#### 49. PHENOMENA CONNECTED WITH LIGHT.

##### Platinum.

1786: 2 Landriani  
 1827: 17 Kastner  
 1846: 20 Schönbein  
 1870: 31 Schinz  
 1871: 22 ———  
 1872: 19 Desains

- 1876: 63 Lallemand  
 1877: 43 Govi  
 1879: 44 Violle  
 1879: 48 Nichols  
 1879: 55 Schwendler  
 1881: 30 Lommel  
 1881: 37 Violle  
 1885: 40 Knoblauch (and palladium)  
 1886: 30 von Aubel  
 1886: 31 von Aubel  
 1887: 18 Duclaux (light on platinum chlorid)  
 1887: 43 Violle  
 1888: 50 Trowbridge and Sabine (and palladium)  
 1888: 51 Weber  
 1888: 53 Kundt  
 1888: 54 Kundt  
 1889: 38 Emden (and palladium)  
 1891: 27 Gladstone (molecular refraction  $\text{IrCl}_4$ )  
 1892: 61 Parmentier  
 1892: 62 Hertz  
 1894: 39 Paschen  
 1895: 33 Gladstone and Hibbert (molecular refraction, chlorid)  
 1895: 41 Macintyre (cyanid screen for X rays)  
 1896: 41 Jackson (do.)  
 1896: 42 Egbert (X rays on platinum)

SPECTRUM.

- 1861: 23 Kirchoff  
 1868: 17 Thalén  
 1879: 47 Gouy

Platinum.

- 1850: 11 Masson  
 1862: 26 Miller  
 1869: 28 Gibbs  
 1877: 44 Ciamician (and palladium)  
 1879: 46 Liveing and Dewar (and palladium)  
 1882: 37 Hartley (and palladium)

Osmium.

- 1863: 17 Frazer

PLATINUM LIGHT UNIT.

- 1884: 25 Siemens  
 1884: 26 Violle  
 1884: 27 ———  
 1885: 43 Trowbridge  
 1886: 33 von Hefner-Alteneck  
 1888: 52 Liebenthal

50. PHENOMENA CONNECTED WITH HEAT.

Platinum.

- 1824: 16 Döbereiner  
 1828: 25 Fischer  
 1828: 26 Schwartz  
 1830: 19 Fischer  
 1841: 18 Fischer  
 1853: 11 Wiedemann and Franz (palladium)  
 1853: 12 Wiedemann and Franz  
 1858: 18 Crace-Calvert and Johnson  
 1872: 20 Buff  
 1878: 60 Rossetti  
 1880: 39 Desains and Curie  
 1882: 43 Poloni  
 1885: 41 Schleiermacher  
 1887: 17 Guldberg (and palladium)  
 1887: 18 Duclaux (heat on platinum chlorid)  
 1887: 44 Bottomley  
 1887: 54 Bottomley  
 1894: 37 Gray

51. THERMO-CHEMICAL PHENOMENA (including specific heat).

- 1861: 22 Regnault  
 1893: 41 Richards

Platinum.

- 1818: 18 Dulong and Petit  
 1819: 9 Dulong and Petit  
 1830: 18 Weber  
 1836: 19 Pouillet  
 1840: 12 Regnault  
 1864: 13 Knopp  
 1877: 45 Violle  
 1882: 31 Hoadley  
 1895: 39 Crompton  
 1895: 40 Bartoli and Stracciati

Platinum alloys with palladium and iridium.

- 1886: 26 Pionchon

Platinum compounds.

- 1864: 13 Kopp  
 1870: 32 Thomsen  
 1871: 21 Thomsen  
 1876: 30 Thomsen  
 1878: 43 Thomsen  
 1880: 38 Berthelot  
 1890: 27 Pigeon  
 1891: 25 Pigeon  
 1891: 26 Pigeon

- 1892: 34 Pigeon  
1894: 10 Pigeon
- Palladium.  
1840: 12 Regnault  
1878: 44 Violle
- Palladium compounds.  
1878: 54 Békétoff (hydrid)  
1880: 38 Berthelot  
1882: 38 Joannis
- Iridium.  
1840: 12 Regnault  
1856: 18 Regnault  
1859: 20 Regnault  
1864: 13 Kopp  
1879: 43 Violle
- Rhodium and osmium.  
1856: 18 Regnault
- Ruthenium.  
1870: 33 Bunsen
52. MAGNETISM of platinum.  
1784: 2 von Sickingen  
1830: 16 Göbel  
1847: 27 Lamont  
1866: 1 Kokscharow  
1880: 44 Hall  
1883: 1a Wilh
53. PHENOMENA CONNECTED  
WITH ELECTRICITY.  
1879: 52 Gore
- Platinum.  
1804: 18 Berthollet  
1816: 3 Dessaignes  
1823: 23 Becquerel  
1824: 17 Dulk  
1826: 16 Marianini  
1827: 21 Despretz  
1827: 22 Harris  
1828: 19 Erdmann  
1828: 27 Pfaff  
1833: 27 Lenz  
1838: 19 Schönbein  
1838: 20 Schönbein  
1838: 21 Andrews  
1840: 13 Jacobi  
1840: 14 Smee  
1841: 21 Jacobi  
1841: 22 Poggendorff  
1845: 21 Poggendorff  
1846: 16 Elsner  
1846: 21 Becquerel  
1851: 13 Becquerel  
1858: 19 Arndtsen  
1858: 20 Matthiessen  
1859: 29 Jacobi  
1864: 15 Raoult  
1869: 31 Obermayer  
1869: 32 Gaugain  
1870: 36 Skey  
1870: 38 Skey  
1870: 39 Edlund  
1871: 27 Skey  
1872: 22 Gaugain  
1873: 28 Volta  
1875: 33 Champion, Pellet and Grenier  
1881: 38 Nichols  
1881: 39 Streintz  
1882: 44 Braun  
1882: 45 Grossens  
1883: 34 Fromme  
1883: 35 Hankel  
1883: 36 Krouchkoll  
1883: 37 Becquerel  
1884: 30 Weiller  
1884: 31 Macfarlane  
1885: 42 Konowalow  
1885: 45 Tomlinson  
1885: 46 Cailliet and Bouty  
1886: 35 Peddie  
1886: 36 Drechsel  
1886: 37 Gautier  
1886: 38 Case  
1887: 56 Preece  
1887: 59 Koozen  
1887: 60 Oberbeck  
1888: 55 Barus (alloys)  
1888: 58 Exner and Turner  
1888: 59 Gore  
1888: 60 Wiedemann and Ebert  
1888: 61 Nahrwold  
1890: 61 Argyropoulos  
1890: 62 Le Chatelier  
1892: 65 Herroun  
1892: 66 Bjerknes  
1893: 42 Paschen  
1893: 43 Rizzio  
1893: 45 Dewar and Fleming  
1894: 40 Neumann  
1895: 36 Engel (copper-platinum couple)
- Palladium.  
1845: 21 Poggendorff  
1846: 21 Becquerel  
1858: 20 Matthiessen  
1869: 33 Villari  
1869: 34 Poggendorff  
1870: 39 Edlund

- 1883: 34 Fromme
- 1884: 29 Knott (hydrid)
- 1886: 34 Knott (hydrid)
- 1893: 45 Dewar and Fleming
- 1894: 40 Neumann

## 54. THERMO-ELECTRICITY.

- 1887: 53 Le Chatelier

## Platinum.

- 1829: 26 Becquerel
- 1855: 24 Adie
- 1876: 62 Knott, MacGregor, and Smith (palladium)
- 1877: 46 Thomsen (and palladium)
- 1878: 56 Gore (and palladium)
- 1880: 40 Bouty
- 1880: 41 Gore
- 1880: 42 Young
- 1880: 43 Blondlot
- 1887: 45 Haga
- 1888: 62 Jahn
- 1892: 64 Barus (with iridium and rhodium)
- 1894: 38 Noll

## 55. POLARISATION PHENOMENA.

## Platinum.

- 1838: 24 Bird
- 1838: 25 Matteucci
- 1839: 11 J. B.
- 1844: 19 Poggendorff
- 1845: 20 Fischer
- 1857: 21 Bertini
- 1859: 28 Schönbein
- 1872: 23 Helmholtz
- 1874: 43 Macaluso
- 1877: 30 Parodi and Mascazzini
- 1878: 55 Morley
- 1878: 57 Beetz
- 1879: 53 Böttger
- 1879: 54 Gladstone and Tribe
- 1880: 45 Helmholtz
- 1882: 46 Streintz
- 1883: 38 Pirani
- 1883: 40 Guëbhard
- 1887: 57 Streintz
- 1887: 58 Fromme
- 1888: 56 Draper
- 1888: 57 Fromme
- 1889: 39 Richarz
- 1890: 60 Arons
- 1890: 63 Richarz
- 1891: 51 Markovsky
- 1891: 52 Burch and Veley

- 1892: 67 Koch and Wüllner
- 1893: 44 Henderson
- 1893: 46 Daniel
- 1893: 47 Koch

## Palladium.

- 1878: 57 Beetz
- 1878: 58 Exner
- 1878: 59 Herwig
- 1879: 53 Böttger
- 1879: 54 Gladstone and Tribe
- 1887: 57 Streintz
- 1887: 58 Fromme

## 56. ELECTROLYTIC PHENOMENA

## —Dissociation.

- 1888: 24 Hampe
- 1894: 24 Mylius and Fromm

## Platinum.

- 1878: 31 Hittorf (chlorid)
- 1878: 32 Morges (chlorid)
- 1879: 15 Drechsel
- 1883: 33 Bartoli and Papasogli
- 1884: 10 Raoult (chlorid)
- 1884: 15 Drechsel (and palladium)
- 1884: 16 Bartoli and Papasogli
- 1886: 12 Foussereau (chlorid and of rhodium)
- 1886: 13 Lehmann (cyanid)
- 1887: 52 Miesler
- 1888: 25 Walden (chlorid and cyanid)
- 1888: 26 Rüdorff (chlorid and cyanid)
- 1889: 19 Ostwald (chlorid)

## Osmium tetroxid.

- 1876: 60 Bleekrode
- 1878: 31 Hittorf

## 57. ALLOYS.

## GENERAL.

- 1826: 11 ———
- 1838: 13 Newton
- 1860: 22 Nicklès
- 1875: 26 Deville and Debray
- 1879: 34 Deville and Mascart
- 1887: 16 Debray
- 1894: 23 Mylius and Fromm
- 1896: 25 Roberts-Austen (diffusion of platinum and rhodium)

## with zinc.

- 1880: 28 Debray (and with lead)
- 1882: 6 Deville and Debray (explosive)

with tin.

1887: 14 Debray

1887: 15 Debray

with iron.

1822: 4 Stodart and Faraday

1878: 41 Boussingault

#### ALLOYS, PLATINUM.

1755: 1 Lewis

1817: 8 Clarke

1817: 9 Clarke

1817: 14 Cooper

1821: 9 Murray

1827: 18 Cooper

1832: 19 ———

1838: 16 Melly

1847: 25 Mention and Wagner

1853: 6 Bolley

1874: 30 Winkler

1881: 31 Bush

1887: 22 Osmond and Werth  
(explosive)

1887: 29 Reinhardt

1888: 55 Barus

1890: 62 Le Chatelier

with potassium.

1822: 3 Murray

with copper.

1797: 2 Mussin-Puschkin

1798: 3 Mussin-Puschkin

1848: 10 Lyons and Millward

1873: 18 H  lonis (bronze)

1885: 26 ——— (brass)

1886: 21 Paillard

1887: 16a Maumen  

with silver

1796: 1 Lampadius

1798: 3 Mussin-Puschkin

1812: 1 Johnson

1814: 7 D'Arcet

1829: 16 Lampadius

1845: 15 Weiger

1878: 19 von J  ptner

1882: 28 Spring

1884: 32 Strouhal and Barus

with gold.

1796: 1 Lampadius

1802: 3 ———

1803: 12 Morveau

1812: 1 Johnson

1819: 2 Gilbert

1824: 2 del Rio

1828: 16 ———

1845: 15 Weiger

1878: 19 von J  ptner

1885: 27 Roessler

1889: 17 Silow

with zinc.

1819: 6 Fox

1838: 14 B  ttger (and with cadmium)

with mercury (platinum amalgam)

1797: 2 Mussin-Puschkin

1797: 3 Richter

1798: 1 Morveau

1799: 5 Mussin-Puschkin

1799: 6 Mussin-Puschkin

1799: 7 Mussin-Puschkin

1803: 13 Mussin-Puschkin

1803: 14 Strauss

1805: 1 Chenivix

1813: 8 Vogel

1814: 6 Schweigger

1821: 8 Daniell

1830: 15 Daniell

1834: 24 B  ttger

1835: 20 Mather

1836: 4 D  bereiner

1850: 12 Joule

1857: 23 Cailletet

1862: 19 Joule

1876: 19 Casamajor

1878: 45 Sabine

1879: 40 Janacek

1884: 11 Krouchkoll

1887: 31 Ostermann and Prip

1888: 27 Crafts

with aluminum.

1822: 3 Murray

with thallium.

1894: 19 Heycock and Neville

with germanium.

1887: 19 Meyer

with tin.

1819: 5 Clarke

1819: 6 Fox

1820: 3 Thomson

with zirconium, glucinum, etc.  
(earths).

1822: 3 Murray

with lead.

1819: 4 Clarke

1867: 14 Deville

1870: 24 Bauer

1871: 24 Bauer

1875: 29 Bauer

1892: 35 Heycock and Neville



with vanadium.

1831: 25 Berzelius

with antimony.

1819: 6 Fox

1822: 3 Murray

with iron.

1775: 1 Morveau

1820: 7 Stodart and Faraday

1838: 13 Schönbein

1867: 15 ———

1875: 3 Deville

1875: 27 Daubrée

1876: 20 Billings

1887: 16a Maumené (and cop-  
per)

with nickel.

1814: 8 Lampadius

1891: 37 ——— ("platinid,"  
with nickel, iron and  
arsenic)

with palladium.

1886: 26 Pionchon

with iridium.

1838: 22 Gaudin

1859: 6 Jacobi

1860: 21 Pelouze

1873: 14 Deville and Debray

1874: 3 Morin

1874: 6 Deville, Debray and  
Morin

1874: 32 Fizeau

1876: 65 Matthey

1876: 66 Deville

1881: 34 Broch, Deville and Stas

1885: 31 Stas

1885: 33 Scharnweber

1885: 45 Tomlinson

1886: 11 Le Chatelier

1886: 26 Pionchon

1888: 41 Klemenčič

1889: 16 Violle

1889: 41 Le Chatelier

1891: 33 Heraeus

1892: 48 Heraeus

with iridium and ruthenium.

1885: 30 Bosscha

PALLADIUM ALLOYS.

with copper.

1848: 10 Lyons and Millward

1886: 21 Paillard

1887: 30 Houston

with silver.

1845: 15 Weiger

with gold.

1827: 13 ———

1845: 15 Weiger

with mercury.

1805: 1 Chenivix

1876: 19 Casamajor

with lead.

1871: 24 Bauer

1892: 35 Heycock and Neville

with iron.

1822: 20 Bréant

IRIDIUM ALLOYS.

1829: 17 Lampadius

1877: 21 Debray

1879: 4 Matthey

with mercury.

1837: 11 Böttger

OSMIRIDIUM.

1879: 35 Van Allen

1882: 5 Debray

1885: 33 Scharnweber

RHODIUM ALLOYS.

1886: 21 Paillard (with copper)

1827: 19 ——— (with gold)

## 58. USE.—General.

Platinum.

1798: 5 Rochon

1800: 7 Rochon

1828: 17 Erdmann

1836: 14 Döbereiner

1836: 15 Trommsdorff

1836: 16 Pelouze

1872: 13 ———

1881: 32 ———

Palladium.

1840: 11 ———

1846: 3 Schmidt and Johnston

Iridium.

1881: 4 ———

1883: 29 Dudley

1885: 25 ———

## 59. PLATINUM CRUCIBLES.

1786: 1 Morveau

1802: 6 Chenivix

1832: 17 Berzelius

1839: 5 Döbereiner

1855: 21 Vogel and Reischauer

1863: 16 Hager

1865: 10 Stahlschmidt, Sy and  
Wagner

1866: 21 Wittstein  
 1868: 12 Vogel  
 1873: 16 Štolba  
 1873: 17 Mohr  
 1874: 33 Smith (gold lined)  
 1892: 5 Heraeus (gold lined)  
 1878: 33 Gooch  
 1888: 39 Morse and Burton  
 1889: 22 von Jüptner  
 1891: 36 Warren  
 1894: 30 Petrzilka

#### Mending crucibles.

1878: 33 Garside  
 1884: 20 Seaman  
 1885: 28 Pratt  
 1885: 29 G. T. H.  
 1889: 40 Pratt

#### Loss of weight of crucibles.

1880: 34 Beilstein  
 1888: 38 Vieth

#### Cleaning crucibles.

1846: 18 Tonnelier  
 1860: 19 Erdmann  
 1860: 20 F. G.  
 1866: 4 Sonstadt  
 1870: 23 Štolba  
 1876: 39 Štolba

#### Removing melt from crucibles.

1876: 38 Stöckmann  
 1888: 34 de Koninck

### 60. PLATINUM VESSELS.

1785: 1 Morveau  
 1787: 1 Morveau  
 1787: 2 Morveau  
 1790: 4 Lavoisier  
 1790: 5 R.  
 1792: 3 Berthollet and Pelletier  
 1813: 6 Neumann  
 1814: 9 Döbereiner  
 1814: 10 Joris  
 1821: 10 Seebeck  
 1828: 23 D'Arcet  
 1830: 13 Faraday  
 1831: 26 Stieren  
 1832: 18 Bischof  
 1844: 16 Pleischl  
 1870: 26 ———  
 1877: 35 Prentice  
 1878: 35 ———

#### Filters.

1857: 18 Mosander  
 1876: 37 Jago  
 1881: 33 Casamajor

1882: 29 Grosjean  
 1882: 30 Casamajor  
 1884: 21 Gawalowski  
 1886: 20 Casamajor  
 1888: 40 Lenz

#### Combustion tubes.

1876: 35 C. J. H. W.  
 1876: 36 Herman  
 1883: 28 Clemence  
 1888: 36 Dudley

#### Concentration apparatus for sulfuric acid.

1866: 22 Scheurer-Kestner  
 1872: 12 Hasenclever  
 1875: 28 Scheurer-Kestner  
 1876: 40 Bode  
 1876: 41 Bode  
 1876: 42 Bode  
 1876: 44 Kessler  
 1876: 45 [Zeman and Fischer]  
 1876: 46 Bode  
 1876: 47 Lamy  
 1877: 33 Bode  
 1877: 34 Bode  
 1878: 36 Kalbfleisch  
 1878: 39 Bode  
 1878: 40 Scheurer-Kestner  
 1880: 35 Scheurer-Kestner  
 1880: 36 Kuhlman  
 1892: 49 Heraeus  
 1892: 51 Burgemeister  
 1892: 54 Lunge  
 1893: 40 Siebert  
 1894: 32 Lunge  
 1892: 52 Weineck (platinum-iridium)

#### Pyrometers.

1803: 11 Morveau  
 1825: 20 ———  
 1825: 21 ———  
 1831: 28 Daniell  
 1862: 17 Becquerel  
 1878: 47 Crova  
 1882: 31 Hoadley  
 1882: 32 Hoadley  
 1882: 33 Hoadley  
 1884: 23 Tremeschini  
 1888: 43 Braun  
 1890: 45 Griffiths  
 1890: 46 Callendar and Griffiths  
 1891: 35 Callendar  
 1892: 53 Callendar  
 1892: 55 Griffiths and Clark  
 1895: 37 Heycock and Neville  
 1895: 38 Appelyard  
 1895: 43 Holborn and Wien

## Coinage.

- 1828: 8 —————  
 1860: 2 Jacobi  
 1872: 16 Jouglet  
 1877: 5 Karmarsch

## Wire.

- 1823: 22 Becquerel  
 1825: 22 ————— (strings for  
                   musical instruments)  
 1840: 10 Fischer (strings for  
                   musical instruments)  
 1877: 28 Gaiffe  
 1885: 36 Read (for telescopes)  
 1886: 24 Banks and Brierley  
           (for singeing)

## Miscellaneous.

- 1859: 21 Jenzsch (triangles)  
 1885: 32 de la Harpe (triangles)  
 1868: 13 Forbes (forceps)  
 1874: 34 Carmichael (digestor)  
 1809: 3 Scott (watch springs)  
 1827: 20 Bréant (siphon)  
 1862: 8 ————— (standard kilo)  
 1876: 51 Luca (lightning-rod  
                   points)  
 1884: 24 Lewis (burner)  
 1885: 33 Scharnweber (carbon  
                   holder)  
 1885: 34 ————— (lamp)  
 1891: 39 Walter (anti-platinum  
                   incandescent lamp)  
 1818: 12 Gay-Lussac (to prevent  
                   bumping)  
 1866: 20 ————— (plated appa-  
                   ratus)  
 1894: 33 Baker & Co. (catalog of  
                   apparatus)  
 1885: 37 Larroque (palladium  
                   hydrogen in photo-  
                   phone)  
 1890: 44 Poland (iridium in in-  
                   candescent lamp)  
 1884: 22 Anders (osmium in tel-  
                   ephone)  
 1841: 20 Johnson (iridosmium  
                   for compass points)

## Platinum chlorid.

- 1834: 16 Kastner (for color  
                   printing)  
 1862: 24 Hunt (for bronzing)  
 1869: 26 Riemann (for indelible  
                   ink)

## Magnesium platino-cyanid.

- 1887: 39 Himly, Leiser and  
           Bardthold (as sym-  
           pathetic ink)

## "Osmic acid" in microscopy.

- 1878: 25 Broesike  
 1878: 26 Pelletan  
 1879: 32 Parker  
 1879: 33 Altmann  
 1880: 21 Certes

61. ACTION OF CHEMICALS on  
platinum (vessels)

- 1846: 19 Faraday (platinum  
                   metals)  
 1811: 4 Davy  
 1892: 48 Heraeus  
 1880: 16 Meyer (sodium and  
                   potassium)  
 1825: 9 Bischof (caustic potash)  
 1879: 13 de Koninck (potash  
                   and soda)  
 1797: 4 Tennant (potassium  
                   nitrate)  
 1798: 2 Morveau (potassium  
                   nitrate)  
 1800: 2 Tennant (potassium ni-  
                   trate)  
 1798: 1 Morveau (potassium  
                   chlorid)  
 1857: 17 Böttger (potassium  
                   chlorate)  
 1831: 24 Buchner (ammonium  
                   nitrate)  
 1817: 7 Vogel (lithia)  
 1818: 11 Vauquelin (lithia)  
 1828: 14 Krälovanszky (lithia)  
 1884: 19 Dittmar (lithia)  
 1878: 40 Scheurer-Kestner (sul-  
                   furic acid)  
 1880: 35 Scheurer-Kestner (sul-  
                   furic acid)  
 1874: 35 Reichardt (silicon)  
 1889: 18 Warren (silicon)  
 1881: 28 Rémont (flame)  
 1845: 14 Kastner (protection  
                   from silica and iron)  
 1847: 9 Claus (caustic potash  
                   and salpeter on iri-  
                   dium)  
 1892: 48 Heraeus (platinum-  
                   iridium)

## 62. PLATING WITH PLATINUM.

- 1803: 14 Strauss  
 1805: 13 Stodart  
 1811: 5 Morveau  
 1819: 7 Howse  
 1828: 20 Zuber  
 1828: 21 Labonté and Depuis  
 1830: 14 Lampadius

1840: 9 Böttger  
 1840: 14 Smee  
 1841: 17 Böttger  
 1841: 19 Elkington  
 1843: 15 Böttger  
 1843: 16 ———  
 1850: 14 Bromeis  
 1853: 8 Jewreinoff  
 1854: 16 Savard  
 1855: 18 Roseleur and Lanaux  
 1855: 19 Böttger  
 1856: 16 Landois  
 1856: 17 Smee  
 1859: 25 Wild  
 1863: 15 ———  
 1864: 12 ———  
 1865: 11 Magnus  
 1866: 20 ———  
 1866: 23 Thomson  
 1866: 24 Böttger  
 1867: 16 Church  
 1867: 17 Church  
 1868: 14 Dodé  
 1869: 23 ———  
 1869: 24 ———  
 1872: 14 Thompson  
 1874: 36 Blain  
 1875: 30 Weiskopf  
 1876: 48 Böttger  
 1877: 31 ———  
 1879: 36 Clerk and Fawsitt  
 1879: 37 Dodé  
 1879: 38 Daumesnil  
 1879: 39 Stoffel  
 1879: 61 Winkler  
 1887: 32 ———

#### Palladium.

1876: 49 Bertrand  
 1876: 50 Frantz

#### Electro-plating with platinum.

1862: 16 Becquerel and Becquerel  
 1886: 22 Thoms  
 1887: 35 Bright Plating Co.  
 1888: 42 Thompson  
 1890: 43 Wahl

#### Iridium.

1887: 33 Dudley  
 1893: 39 Dudley

#### DEPOSITION ON GLASS: platinum.

1828: 18 Erdmann  
 1828: 22 Schweigger  
 1829: 24 Döbereiner  
 1853: 7 Böttger  
 1859: 22 Dullo

1859: 23 Elsner  
 1859: 24 Vasserot (and palladium)  
 1865: 12 Salvétat  
 1865: 13 Dodé  
 1865: 14 ———  
 1865: 15 Schwarz  
 1865: 16 Weiskopf  
 1867: 18 Böttger  
 1869: 22 Böttger  
 1869: 25 Hoffman  
 1870: 27 Jouglet  
 1873: 19 Dodé  
 1873: 20 Röntgen  
 1877: 32 Wright  
 1887: 34 ———  
 1888: 44 von Uljanin  
 1889: 23 ———

#### 63. PIGMENT for porcelain painting.

##### Platinum.

1802: 7 Klaproth  
 1821: 11 Charlton  
 1821: 12 Charlton  
 1822: 5 ———  
 1828: 24 Kastner  
 1831: 29 St. Amand  
 1847: 24 Lüdersdorff  
 1849: 11 Salvétat  
 1857: 22 Müller  
 1870: 28 Schwarz  
 1875: 31 Heyl  
 1876: 52 ——— (Pflug's Farbe)  
 1877: 36 Kümmel  
 1885: 35 Roessler (and palladium)  
 1887: 36 Erlich and Storek  
 1887: 37 Erlich and Storek  
 1887: 38 Schwarz

##### Iridium.

1821: 12 Charlton  
 1833: 26 Frick  
 1868: 15 Frick  
 1885: 35 Roessler

#### 64. USE IN PHOTOGRAPHY.

1872: 21 Merget

##### Platinum.

1856: 14 Caranza  
 1874: 42 Willis  
 1879: 41 Koninck  
 1879: 42 ———  
 1880: 17 Eder  
 1880: 37 Fabre

1881: 35 —————  
 1885: 38 Needham  
 1886: 25 Vogel  
 1887: 46 —————  
 1887: 47 Pizzighelli  
 1887: 48 Pringle  
 1887: 49 Willis  
 1887: 50 Bory  
 1887: 51 —————  
 1888: 45 Vidal and Vogel  
 1888: 46 Reynolds  
 1889: 28 —————  
 1889: 30 von Brühl  
 1889: 31 Schnauss  
 1889: 32 —————  
 1889: 33 Eder  
 1889: 34 —————  
 1889: 35 Crawford  
 1889: 36 Mercier  
 1889: 42 Pizzighelli  
 1890: 47 Liesegang  
 1890: 48 Perkins  
 1890: 49 Clark  
 1890: 50 Gastein  
 1890: 51 —————  
 1890: 52 Lenhard  
 1890: 53 Masse  
 1890: 54 Blanchard  
 1890: 55 Harrison  
 1890: 56 —————  
 1891: 42 Brunel  
 1891: 43 Stieglitz  
 1891: 44 Hezekiel  
 1891: 45 Eder  
 1891: 46 Huszar  
 1891: 47 Burton  
 1892: 56 Eder and Valenta  
 1892: 58 Pizzighelli  
 1892: 59 Willis  
 1892: 60 Nichol

## Palladium.

1890: 47 Liesegang  
 1890: 48 Perkins  
 1891: 48 Fourtier  
 1891: 49 Pilet  
 1892: 57 Fourtier  
 1896: 36 Kelly and Hamley

## Iridium.

1874: 42 Willis  
 1889: 36 Mercier  
 1890: 47 Liesegang  
 1890: 57 Berthiot  
 1890: 58 —————

## Osmium.

1889: 36 Mercier  
 1890: 47 Liesegang

## IMITATION OF PLATINUM.

1830: 17 —————  
 1836: 20 —————

## 65. EXHIBITS AT EXPOSITIONS.

1862: 23 —————  
 1863: 1 Marsh  
 1863: 4 Tunner  
 1867: 2 Wagner  
 1873: 4 Raymond  
 1874: 4 Beilstein  
 1878: 2 —————  
 1894: 31 Lunge  
 1895: 3 Andreoli

## 66. BIBLIOGRAPHY.

1883: 1 Claus (platinum met-  
           als)  
 1872: 7 Bolton (magnesium  
           platinocyanid)  
 1885: 23 Perry (iridium)

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# REVIEW AND BIBLIOGRAPHY

OF THE

## METALLIC CARBIDES

BY

J. A. MATHEWS, M. S., M. A., F. C. S.



CITY OF WASHINGTON  
PUBLISHED BY THE SMITHSONIAN INSTITUTION  
1898



## LETTER OF TRANSMITTAL

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WASHINGTON, APRIL 5TH, 1897.

The Committee on Indexing Chemical Literature, appointed in 1882 by the American Association for the Advancement of Science, has voted to recommend to the Smithsonian Institution for publication the following : —

REVIEW AND BIBLIOGRAPHY OF THE METALLIC CARBIDES,

by J. A. Mathews, M. S., M. A., School of Mines, Columbia University, New York.

H. CARRINGTON BOLTON, *Chairman.*

MR. S. P. LANGLEY,

*Secretary of the Smithsonian Institution.*



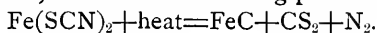


## INTRODUCTION.

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Most of the literature of the metallic carbides is of recent date, yet the beginnings of the studies upon compounds of carbon with metals take us back to the very dawn of the present century, for during its first years chemists described such compounds. The relation of carbon to iron in steel was said to be that of a true chemical compound as early as 1800, and in 1808 Davy prepared the carbide of potassium. At intervals from that time to the present new carbides have been described.

In looking over the old references one cannot but notice that, with few exceptions, the carbides described therein are of those metals concerning which there is to-day the greatest doubt as to their forming such compounds at all. For example, about sixty years ago a general method was given for forming the carbides of iron, copper, lead, zinc, bismuth, silver, tin, and manganese by heating in a retort their sulphocyanides, air being excluded during the operation. It was said that sulphide of carbon and nitrogen were evolved; the reactions working parallel to this:—



The preceding list contains at least four elements which are not, at this time, supposed to form carbides. Frequent mention of other carbides is made in old works on chemistry. In the light of recent investigation these seem of doubtful worth, as the compounds mentioned find no place in modern works, or else their existence has been denied. Some of these old references are given later without comment as to their value, the reader being free to accept or reject any of them.

In consideration of the interest manifested by chemists recently in this class of bodies, it seems that a brief review of the work done to date may be of considerable interest to the general reader; while this, in conjunction with the bibliographical references, it is hoped may be of some value to the chemical student or investigator. With these two ends in view the following pages were compiled.

The general plan has been to give a very condensed account of the methods of preparation, physical and chemical properties of the carbides now known, considering them in alphabetical order. Following each descriptive portion are the references to the literature bearing thereon. The titles of original papers are in most cases given in full, that the scope of the article may be judged therefrom. Minor articles and abstracts are

also largely given ; in this way the value of the bibliography is increased to those who have not ready access to extensive reference libraries, since the same matter is referred to as given in various publications, to one or another of which most chemists have access.

Within the last five years the renewed attention of chemists has been turned toward this class of compounds, and new carbides have been produced in rapid succession. Experiments upon the reduction of metallic oxides by means of carbon in an electric furnace have resulted in the production of many of the newly discovered carbides. In studying the literature of these compounds, the work of one man is especially noticeable. More than to all other chemists together is praise due M. Henri Moissan for the untiring energy with which he has investigated the carbo-metallic compounds. So often has he astonished chemists with the results of his electro-chemical experiments, that new discoveries by him are likely to be considered as a matter of course. M. Moissan's work upon artificial diamonds is one of the greatest achievements of science in imitating nature's methods.

In conducting his experiments Moissan makes use of an electric furnace of very simple construction. It consists of a limestone block in the upper surface of which is chiseled a rectangular cavity, which is lined with a coating of magnesia and of carbon. Through opposite sides of the block are inserted stout carbon electrodes, and through one of the other sides is an opening through which a carbon tube is inserted. In this tube the materials to be heated are placed and thus inserted into the arc. It is estimated that a temperature of  $4000^{\circ}$  is obtained in this furnace. Before using the furnace it is covered with another piece of limestone, on the lower side of which are layers of magnesia and carbon, which fit into or cover the cavity of the lower block. So poorly do these materials conduct heat that the hand may be kept on the outside of the furnace for several minutes after the current is started.

The literature of the metallic carbides is as yet confined to periodicals. Following the main portion of this paper is given an author's index, together with the elements to the literature of whose carbides each has contributed. By referring back to the page upon which such carbides are discussed the full references will be found. Below are given a few references having a general bearing upon the carbides.

MOISSAN. "Sur un nouveau modèle de four électrique à réverbère et à électrodes mobiles." C. R. 117, p. 679.

MOISSAN. "Cristallisation du carbon sous l'action d'un dissolvant métallique." Bull. Soc. Chim. (1895) [3] 13, p. 808.

MAISSON. "Sur la formation des carbures d'hydrogène gazeux et liquides par l'action de l'eau sur les carbures métalliques. Classification des carbures." Bull. Soc. Chim. (1896) [3], 16, p. 1284, or C. R. (1896) p. 1462, or Ztschr. Elektrochem. (1896) p. 134.

MOISSAN (concerning those carbides which are decomposed by cold water). Ann. de chim. [7] 9, p. 302 ; or Chem. Centrbl. (1896) pt. 2, p. 1082.

BORCHERS. "Die elektrischen Ofen zur Metallgewinnung, u. s. w." Ztschr. Elektrochem. (1896) p. 189 and p. 213.

AHRENS. "Die Metallcarbide und ihre Verwendung." Sammlung chemischer und chemisch-technischer Vorträge, vol. I, part 1, 1896.

With this explanatory introduction the following pages will, it is hoped, be clear to all whose interest in the metallic carbides leads them to consult this, — a bibliographical dictionary of those compounds.

J. A. MATHEWS.

CHEMICAL DEPARTMENT,  
COLUMBIA UNIVERSITY,  
January, 1897.

NOTE. — During the period since the manuscript of the present work was submitted there has appeared a great deal of original material upon the carbides. Especially must be noted a number of books, and the addition of these, together with the more important journal references, will add very materially to the usefulness of this bibliography.

*Book References: —*

AHRENS. Handbuch der Elektrochemie, Stuttgart, 1896.

MOISSAN. Le Four électrique, Paris, 1897. 385 pages.

ZETTEL. Authorized German translation of the above. Berlin, 1897, 360 pages.

PANAOTOVIC. Calciumcarbid und Acetylen, in Vergangenheit, Gegenwart und Zukunft. Leipzig, 1897, 8vo.

PICTET. L'Acétylène. Son passé, son présent, son avenir. Genève, 1896, 8vo.

PELLISSIER. L'Eclairage à l'acétylène. Paris, 1897, 8vo.

PERRODIL. Le carbure de calcium et l'acétylène. Les Fours électriques. Paris, 1897, 16mo.

LEFEVRE. Carbure de calcium et l'acétylène. Paris, 1898, 12mo.

*Journal References: —*

( $\text{Al}_4\text{C}_3$ .) MOISSAN. Ann. de chim. [7] 9, p. 302. (From  $\text{CaC}_2$  and alumina) C. R. (1897) CXXV, p. 839.

( $\text{BaC}_2$ .) BULLIER. Ber. d. chem. Ges. XXVIII, ref. p. 41.

( $\text{CaC}_2$ .) MOISSAN. Nouvelle méthode de préparation des carbures par l'action du carbure de calcium sur les oxyds. C. R. (1897) CXXV, p. 839.

YVON. De l'emploi du  $\text{CaC}_2$  pour la préparation de l'alcool absolu. C. R. (1897) CXXV, p. 1181.

LE CHATELIER. Sur les impuretés des carbures de calcium commercial. Bull. Soc. Chim. (1897) [3] XVII, p. 793.

WARREN. ( $\text{CaC}_2$  as a reducing agent.) Chem. News (1897) 75, p. 2. J. Chem. Soc. (1897) LXXII, p. 212.

( $\text{CeC}_2$ .) MOISSAN. Bull. Soc. Chim. (1897) [3] XVII, p. 261.

( $\text{Cr}_4\text{C}$  and  $\text{Cr}_3\text{C}_2$ .) MOISSAN. C. R. (1897) CXXV, p. 839.

(Iron carbides.) HANS FREIHERR VON JÜPTNER. Kohlenstoffformen im Eisen. Sammlung chemischer und chemisch-technischer Vorträge, Vol. I, parts 11 and 12 (1896).

MOISSAN. Préparation du carbure de fer par union directe de métal et du carbone. C. R. (1897) CXXIV, p. 716. Bull. Soc. Chim. (1897) [3] XVIII, p. 540. J. Chem. Soc. (1897) LXXII, p. 375.

- MYLIUS, FOERSTER, SCHOENE. Ueber das Carbid des geglühten Stahls. Ber. d. chem. Ges. (1897) XXIX, p. 2991. Bull. Soc. Chim. (1897) [3] XVIII, p. 531.
- (LaC<sub>2</sub>.) PETERSSON. Ber. d. chem. Ges. (1896) XXVIII, p. 2432.
- MOISSAN. Chem. News (1896) 74, p. 84. Ber. d. chem. Ges. (1897) XXIX, ref. p. 618.
- (Li<sub>2</sub>C<sub>2</sub>.) MOISSAN. Bull. Soc. Chim. (1897) [3] XVII, p. 260. Ber. d. Chem. Ges. (1897) XXIX, ref. p. 210.
- GUNTZ. C. R. (1896) CXXIII, p. 1273. J. Chem. Soc. (1897) LXXII, p. 212.
- (Mn<sub>3</sub>C.) MOISSAN. Chem. News (1896) 73, p. 141. Ber. d. chem. Ges. (1897) XXIX, ref. pp. 266 and 614. C. R. (1897) CXXV, p. 839.
- (Mn<sub>2</sub>C.) MOISSAN. C. R. CXXII, p. 1462. Ber. d. chem. Ges. (1897) XXIX, ref. p. 614. C. R. (1897) CXXV, p. 839.
- (SiC.) RINNE. Jsb. f. Mineral. (1897) II, p. 1-27. Chem. Centrbl. (1897) Bd. II, p. 724.
- MOISSAN. (From SiO<sub>2</sub> and CaC<sub>2</sub>.) C. R. (1897) CXXV, p. 839.
- FITZGERALD. (Upon the development of the CSi industry.) J. Frankl. Inst. 143, p. 81. J. Am. Chem. Soc. (abs.) (1897) XIX, p. 36.
- (Na<sub>2</sub>C<sub>2</sub>.) MATIGNON. Propriétés du carbure de sodium. C. R. (1897) CXXV, p. 1033. (NaHC<sub>2</sub>) C. R. (1897) CXXIV, pp. 775 and 1026. Bull. Soc. Chim. [3] XVIII, p. 540.
- DE FORCRAND. (Heat of formation.) C. R. (1897) CXXIV, p. 1153. Bull. Soc. Chim. (1897) [3] XVIII, p. 726.
- (TiC.) MOISSAN. C. R. (1897) CXXV, p. 839. (From TiO<sub>2</sub> and CaC<sub>2</sub>).
- (W<sub>2</sub>C.) MOISSAN. C. R. (1897) CXXV, p. 839.
- (Ur<sub>2</sub>C<sub>3</sub>.) MOISSAN. Bull. Soc. Chim. (1897) [3] XVII, p. 12. Ber. d. chem. Ges. XXIX, ref. p. 207.
- (VaC.) MOISSAN. Ber. d. chem. Ges. XXIX, ref. p. 580. Chem. News (1896) 74, p. 29.
- (ZrC<sub>2</sub>.) TROOST. Ber. d. chem. Ges. XXVI, ref. p. 483.
- (ZrC.) MOISSAN and LENGFELD. Ber. d. chem. Ges. (1897) XXIX, ref. pp. 343 and 614. Chem. News (1896) 74, p. 175.

These additions include the more important contributions to the literature of the carbides during 1897, together with a few from the latter part of 1896, which, with the main portion of this paper, constitute a nearly complete bibliography of these compounds.

THE AUTHOR.

March, 1898.

## LIST OF ABBREVIATIONS.

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- Allg. J. Chem. — (Scherer's) Allgemeines Journal der Chemie (1798-1810).  
 Am. Chem. J. — American Chemical Journal (1879-96+).  
 Am. Drug. and Pharm. Rec. — American Druggist and Pharmaceutical Record (New York).  
 Am. Gas-Light J. — American Gas-Light Journal.  
 Am. J. Sci. — American Journal of Science (1818-96+).  
 Ann. Chem. — (Wöhler and Liebig's) Annalen der Chemie und Pharmacie (1840-73), (and Liebig's) Annalen der Chemie (1874-96+).  
 Ann. de chim. — Annales de chimie et de physique (1789-1896+).  
 Ann. Mines. — Annales des mines (1817-96+).  
 Ann. der Pharm. — Annalen der Pharmacie (1832-39).  
 Ann. Phil. — Annals of Philosophy (1813-26).  
 Ann. der Phys. — Annalen der Physik (Gilbert, 1799-1824) and Annalen der Physik und Chemie (Poggendorff, 1824-77).  
 Ber. d. chem. Ges. — Berichte der deutschen chemischen Gesellschaft (1868-96+).  
 Bull. Acad. Belg. — Bulletin de l'Académie Royale des Sciences, des Lettres, et des Beaux-Arts de Belgique.  
 Bull. Soc. Chim. — Bulletin des Séances de la Société chimique de Paris (1864-96+).  
 Chem. Centrbl. — Chemisches Centralblatt (1856-96+).  
 Chem. News. — Chemical News (London).  
 C. R. — Comptes rendus hebdomadaires des Séances de l'Académie de Sciences (Paris, 1835-96+).  
 D. R. P. — Deutsches Reichspatent.  
 Jsb. Pharm. — Jahresbericht der Pharmacie.  
 Jsb. Chem. — Jahresbericht über die Fortschritte der Chemie, u. s. w. (1847-90+).  
 J. Am. Chem. Soc. — Journal of the American Chemical Society (1876-96+).  
 J. Chem. Soc. — Journal of the Chemical Society (London, — Proceedings, Abstracts, and Transactions. 1849-96+).  
 J. f. Gasbeleucht. — Journal für Gasbeleuchtung.  
 J. Frankl. Inst. — Journal of the Franklin Institute (Philadelphia).  
 J. Soc. Chem. Ind. — Journal of the Society of Chemical Industry (1882-96+).  
 J. prakt. Chem. — Journal für praktische Chemie (1834-96+).  
 J. I. and S. Inst. — Journal of the Iron and Steel Institute.  
 N. J. der Pharm. — Neues Journal der Pharmacie für Aertze, u. s. w. (Trommsdorff, 1817-34).  
 Oesterr. J. Berg- u. Hüttenwesen. — Oesterreiches Journal für Berg- und Hüttenwesen.  
 Phil. Trans. — The Philosophical Transactions of the Royal Society of London (1665-1896+).  
 Polyt. Centrbl. — Polytechnisches Centralblatt (1835-73).  
 Proc. Chem. Soc. — Proceedings, see under Journal of the Chemical Society (London).

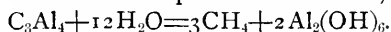
- Proc. Inst. Mech. Eng. — Proceedings of the Institute of Mechanical Engineers.  
Recueil trav. chim. Pays-Bas. — Recueil des Travaux chimiques des Pays-Bas (Leiden, 1882-94+).  
School Mines Q. — School of Mines Quarterly (New York, 1879-96+).  
Trans. Am. Inst. M. Eng. — Transactions of the American Institute of Mining Engineers.  
U. S. Geol. Sur. — Bulletins of the United States Geological Survey.  
U. S. Pat. — United States patent.  
Ztschr. anorgan. Chem. — Zeitschrift für anorganische Chemie (1892-96+).  
Ztschr. angew. Chem. — Zeitschrift für angewandte Chemie (1887-96+).  
Ztschr. Chem. Pharm. — Zeitschrift für Chemie und Pharmacie.  
Ztschr. Elektrochem. — Zeitschrift für Elektrochemie.  
Ztschr. Krystall. — Zeitschrift für Krystallographie und Mineralogie (1877-96+).

# REVIEW AND BIBLIOGRAPHY OF THE METALLIC CARBIDES.

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## ALUMINUM AND CARBON.

Moissan has prepared a carbide of aluminum (1) from kaolin and carbon, and (2) from metallic aluminum and carbon. The method employed was to put the Al in a carbon boat and heat for five to six minutes in the electric furnace. Hydrogen was passed through the carbon tube of the furnace both during heating and while cooling. A current of 300 amperes and 65 volts was used. From this process results a mixture of Al and  $\text{Al}_4\text{C}_3$ . The  $\text{Al}_4\text{C}_3$  consists of yellow, transparent crystals; sp. gr. 2.36; decomposed at red heat by Cl or Br, leaving a residue of amorphous carbon. Water decomposes it in the cold, thus: —



### LITERATURE.

- MOISSAN. Préparation d'un carbure d'aluminium cristallisé. C. R. (1894) v. 119, p. 16, or Bull. Soc. Chim. [3] 11, p. 1010, or Abs. J. Chem. Soc. (1894) 66, pt. 2, p. 450, Chem. Centrbl. (1894) 65, pt. 2, p. 268. *See also*  
MOISSAN. Réduction de l'alumine par le charbon. C. R. (1894) 119, p. 935, or Abs. J. Chem. Soc. (1895) 68, pt. 2, p. 226.  
DEVILLE. Ann. de Chim. [3] 45, p. 15.  
MALLET. Ueber Stickstoffaluminium und die Einwirkung von Aluminium auf Kohlenstoffkalium bei höher Temperatur. Ann. Chem. 186, p. 155.

## ALUMINUM, BORON, AND CARBON.

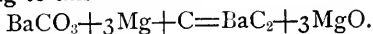
A very refractory substance, to which the formula  $\text{Al}_3\text{C}_2\text{B}_{48}$  has been given, is interesting because of its great hardness, between corundum and diamond.

### LITERATURE.

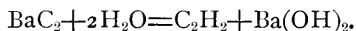
- HAMPE. Ueber das Bor. Ann. Chem. (1876) 183, p. 75. *See also*  
WÖHLER AND ST. C. DEVILLE. Ann. Chem. 101, ps. 113 and 347.

## BARIUM AND CARBON.

The carbide of barium may be made in the electric furnace in the same way as calcium carbide (q. v.). It also results by heating together  $\text{BaCO}_3$ , Mg and C according to this reaction: —



In the electric furnace either  $\text{BaCO}_3$  or  $\text{BaO}$  may be employed.  $\text{BaC}_2$  forms dark colored crystals, sp. gr. = 3.75, decomposed by water, thus:—



At high temperatures the carbides of the alkaline-earths react violently with the halogens.

#### LITERATURE.

MAQUENNE. Sur un carbure défini du baryum. C. R. 114, p. 361.

MAQUENNE. Sur une nouvelle préparation de l'acétylène. C. R. (1892) 115, p. 558.

BULLIER. Deutsches Reichspatent, 77,168.

MOISSAN. Etude des acétylures cristallisés de baryum et de strontium. C. R. (1894) 118, p. 683, or Chem. Centrbl. (1894) 65, pt. 1, p. 856, or Bull. Soc. Chim. [3] 11, p. 1007.

#### BORON AND CARBON.

Two carbides of boron have been described,  $\text{BC}$  or  $\text{B}_2\text{C}_2$ , and  $\text{B}_6\text{C}$ . According to Moissan two compounds are formed in the electric furnace, one of which is permanent and resists the action of  $\text{KClO}_3 + \text{HNO}_3$ , while the other compound is broken down by this treatment. He has given the more stable compound the formula  $\text{B}_6\text{C}$ . It is produced when boron and certain boron compounds are heated with carbon in the electric furnace. Black, shining crystals, sp. gr. 2.51, harder than carborundum, and with it new facets may be cut upon diamonds.  $\text{Cl}$  at high temperatures decomposes it with deflagration, chloride of boron and carbon resulting. Very slowly oxidized at  $1000^\circ$ , it is not acted upon by mineral acids, nor by S, P, N, Br, or I.

Mühlhäuser heated together in an electric furnace boric-anhydride and carbon. The product he treated twice with hot  $\text{HCl}$ , then with  $\text{HF}$ , and  $\text{H}_2\text{SO}_4$ . There remained a graphite-like mass, which by analysis showed the composition  $\text{BC}$  or  $\text{B}_2\text{C}_2$ . The compound is fusible at a high temperature and is decomposed by fusion with alkali.

#### LITERATURE ( $\text{B}_6\text{C}$ ).

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MOISSAN. Préparation et propriétés du borure de carbone. C. R. (1894) 118, p. 556, or Abs. J. Chem. Soc. (1894) 66, pt. 2, p. 279, or Bull. Soc. Chim. (1894) [3] 11, p. 998. *See also*

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WÖHLER and ST. C. DEVILLE. Ann. de chim. (1858) [3] 52, p. 63.

( $\text{B}_2\text{C}_2$ ) MÜHLHÄUSER. Ztschr. anorgan. Chem. 5, p. 92, or Chem. Centrbl. (1893) 64, pt. 2, p. 747, or Abs. J. Chem. Soc. (1893) 64, pt. 2, p. 570.

#### CALCIUM AND CARBON.

In 1862 Wöhler gave a method of producing acetylene gas from a compound of calcium and carbon. This compound was prepared from a zinc-



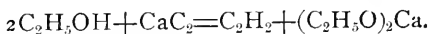
calcium alloy by heating with carbon. Wöhler gave some of the properties of the carbide which resulted. In 1893 Travers recorded another method of preparing calcium carbide, and in the following year Moissan produced it in his electric furnace, both from  $\text{CaCO}_3$  and from  $\text{CaO}$  heated with sugar carbon. About the same time the Willson Aluminum Company, in this country, while experimenting upon the reduction of the alkali earths by means of carbon, found that carbide of calcium was formed, although when first produced the compound was not recognized by them, but was considered as a waste product. As soon as its properties were learned, Willson took out patents for its production in this country. Bullier holds a German patent for the production of Ca-, Ba-, and Sr-carbides, although the method patented is said to be of Moissan's discovery. The carbides of calcium and silicon seem thus far to be the only carbides of commercial value in themselves. The value of calcium carbide lies in its ready decomposition with water, yielding nearly pure acetylene gas, which under proper conditions is unexcelled as an illuminating gas. When made upon a commercial scale, calcium carbide is produced from lime and coke. The cost of production is still rather high, and the chances of acetylene gas being generally introduced for lighting purposes in the immediate future are not very bright. In time the necessary improvements may be made which will do away with present difficulties. The cost of the electric power is the chief obstacle now.

$\text{CaC}_2$  forms in opaque, brownish-red crystals, sp. gr. 2.22. It is quite insoluble in most of the ordinary solvents in the cold. Dry hydrogen is without action in the cold and seems to be without effect even when hot upon the pure calcium carbide. The commercial article may contain tarry products which a stream of dry hydrogen will drive out. Air acts in about the same way as hydrogen. At a very high temperature a sample, submitted to the action of a stream of oxygen, glows and is partly oxidized.

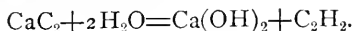
$\text{HCl}$  (gas) decomposes it when hot.  $\text{Cl}$  and  $\text{Br}$  at even moderate temperatures cause the sample to glow brightly, to swell up, and then fuse together. Very slight action in the cold when treated with  $\text{H}_2\text{SO}_4$ , but by heating the action is increased and a gas is evolved which burns with a luminous flame.

With a mixture of  $\text{H}_2\text{SO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  calcium carbide reacts violently, vigorous oxidation taking place. Little or no  $\text{C}_2\text{H}_2$  is evolved in the above reaction.

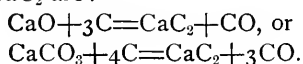
With strong  $\text{HNO}_3$  there is an evolution of brown fumes and a gas which burns with a smoky flame. Glacial acetic acid slowly decomposes it. By fusion with  $\text{NaOH}$  this carbide is decomposed and a gas is evolved which is probably acetylene. At  $180^\circ\text{C}$  calcium carbide is decomposed by alcohol, thus :—



The simple reaction with water is :—



Moist air slowly effects this decomposition. Since it is the decomposition product of this carbide which makes it valuable we include below some references to acetylene, its properties, production, etc. The equations for the production of  $\text{CaC}_2$  are:—



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### CERIUM AND CARBON.

A carbide of the composition  $\text{CeC}_3$  results by heating cerium formate or oxalate in an apparatus from which the air is excluded. When the residue from this operation is extracted with  $\text{HCl}$  a compound remains of the above composition, which is not soluble even in hot, concentrated acids. Many chemists doubt the existence of this compound.

The carbide which Moissan has produced in the electric furnace has the formula  $\text{Ce}_2\text{C}$ . It is prepared from  $\text{CeO}_2$  and sugar carbon. It forms transparent crystals, sp. gr. 5.23. When acted upon by water it is decomposed, evolving  $\text{C}_2\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ , and the residue extracted with ether contains a small amount of fluid and solid hydrocarbons. The reaction must obviously be very complex.

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### CHROMIUM AND CARBON.

When chromium is heated in an electric furnace for ten to fifteen minutes with a large excess of carbon, with a current of 70 volts and 350 amperes, there is produced  $\text{Cr}_3\text{C}_2$ ; brilliant laminae, greasy lustre, sp. gr. 5.62, not acted upon by concentrated or dilute  $\text{HNO}_3$  or aqua regia. Fused  $\text{KNO}_3$  attacks it vigorously, not so  $\text{KOH}$ . It is not decomposed by  $\text{H}_2\text{O}$ , hot or cold. It is harder than the topaz. Somewhat soluble in dilute  $\text{HCl}$ .

$\text{Cr}_4\text{C}$  obtains as long, shining needle-like crystals which are found upon

the surface of ingots of metallic Cr or in cavities existing in such ingots. It is harder than quartz; sp. gr. 6.75; melts at a higher temperature than Pt. One of the above carbides is also said to result by passing  $\text{CS}_2$  vapors over hot Cr. Certain compounds of Fe, Cr, and C are known, such as  $\text{Fe}_7\text{Cr}_2\text{C}_3$  and  $\text{Cr}_3\text{FeC}_2$ .

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## COBALT AND CARBON.

Over thirty years ago Thompson described a compound containing about 4% C, which was very hard and brittle, of bismuth color, sp. gr. 8.43. It was made by heating  $\text{Co}_2\text{O}_3$  and argol in a closed carbon crucible for several hours.

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## COLUMBIUM AND CARBON.

A double compound of columbium carbide and nitride of this composition,  $3\text{CbC}_2\text{CbN}$ , has been mentioned by Joly.

## LITERATURE.

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## COPPER AND CARBON.

An explosive compound to which various formulas have been given results by passing acetylene through ammoniacal copper solutions. Very little carbon is taken up by direct heating of copper and carbon. A little copper is said to be taken up in combination during the poling process of refining copper. Some very good work has been done recently upon the acetylids in this country and England, but with not altogether accordant results. The formulas usually given for copper acetylide are  $\text{C}_2\text{Cu}_2$  and  $\text{C}_2\text{Cu}_2 + \text{H}_2\text{O}$ . See especially *Keiser*, *Am. Chem. J.* 14.

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## GLUCINUM AND CARBON.

P. Lebeau describes the preparation of a compound to which he gives the formula  $\text{Gl}_4\text{C}_3$ . Henry advances the formula  $\text{Gl}_2\text{C}$  for Lebeau's compound. It is prepared by heating for ten minutes a mixture of glucinum oxide and carbon (Zuckerkohle); the current used was 950 amp., 40 volts. With a weaker current a nitrogen-containing compound results.  $\text{Gl}_4\text{C}_3$  forms fine crystals, sp. gr. = 1.9, brownish-yellow color, and resembling  $\text{Al}_4\text{C}_3$  in many of its properties. It is very hard, and by decomposition with  $\text{H}_2\text{O}$  methane is produced.

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## IRIDIUM AND CARBON.

$\text{IrC}_4$  results by heating thin strips of iridium in the alcohol flame. The product forms a velvet-black coating. It is inflammable, and burns, leaving a residue of Ir. The oxide of Ir heated in the presence of some hydrocarbons yields  $\text{IrC}_4$ , with a display of incandescence. (Berzelius.)

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## IRON AND CARBON.

The subject of carbon in iron and steel has been extensively discussed, but not always from a chemical standpoint. The mechanical effect of carbon in iron and steel is studied often without taking into consideration

the condition in which that carbon exists ; but the carbides of iron, as such, — as definite chemical compounds, have not been so widely written upon. The point of view from which the subject is often studied seems so different from the view in which the other carbides are here considered, that we do not feel justified in going into the literature exhaustively from all standpoints, yet the references given below cover a broad consideration of the subject.

A great many compounds of Fe and C have been mentioned by different chemists, but the existence of some of them is doubtful. Some of these are  $\text{Fe}_{24}\text{C}$ ,  $\text{Fe}_3\text{C}$ ,  $\text{Fe}_4\text{C}$ ,  $\text{Fe}_5\text{C}$ ,  $\text{Fe}_3\text{C}_3$ , and  $\text{Fe}_2\text{C}$ , beside some compounds of three or more elements, such as  $\text{Fe}_7(\text{CrMo})_5\text{C}_4$ ,  $\text{Fe}_7(\text{CrW})_8\text{C}_4$  and  $\text{Cr}_2\text{Fe}_7\text{C}_3$ , and  $\text{Cr}_3\text{FeC}_2$ .

$\text{Fe}_4\text{C}$  is a dark-gray, fusible crystalline substance, formed directly from Fe and C at a high temperature. The formula  $\text{Fe}_{24}\text{C}$  has been given to high carbon steel.

$\text{Fe}_3\text{C}$  occurs in all kinds of malleable iron, and remains behind after treating the iron with a 10%  $\text{H}_2\text{SO}_4$  solution, the operation being conducted with the air excluded. That the subject of carbon in iron has been long studied will be seen from the following references. Many of these are of little value to those studying the chemistry of steel, etc., and having the advantages of access to the modern reports upon the subject. We arbitrarily divide the literature into the old and the recent.

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- DE BENNEVILLE. A study of some alloys with iron carbides, mainly tungsten and manganese. Jour. of the Iron and Steel Inst. (1896) no. 1.

## LANTHANUM AND CARBON.

$\text{C}_2\text{La}$  has been made from lanthanum oxide and sugar-carbon. These heated for ten minutes in the electric furnace under the action of a current of 350 amp. and 50 volts combine to form yellow crystals, sp. gr. 5.02. This carbide is decomposed by water, yielding  $\text{C}_2\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ , and leaving a residue of fixed hydrocarbons. The carbide appears golden yellow on a fresh fracture. It is attacked by the atmospheric moisture Pettersson gives  $\text{H}_2$  and  $\text{C}_2\text{H}_2$  as the decomposition products.

## LITERATURE.

- O. PETTERSSON. Kohlenstoffverbindungen von den Metallen der seltenen Erden. Ber. d. Chem. Ges. (1895) 28, p. 2419, or Chem. Centrbl. 66, pt. 2, p. 960, or Abs. J. Chem. Soc. (1896) 70, pt. 2, p. 25.
- MOISSAN. Etude du carbure de lanthane. C. R. 123, p. 148, or Zeitschr. Elektrochem. (1896) III, p. 108, or Chem. Centrbl. (1896), pt. 1, p. 731, or Bull. Soc. Chim. (1896) [3] 16, p. 1293.

## LEAD AND CARBON.

Certain old chemistries mention the existence of a compound of lead and carbon. No carbide of lead has been made as yet in the electric furnace, and the same is true of tin, bismuth, and gold.

## LITERATURE.

- GMELIN. Handbook of Chemistry (Watt's translation), V, p. 122.
- JOHN. Berlinisches Jahresbericht der Pharmacie (1820) p. 320.
- BERZELIUS. Lehrbuch der Chemie (1836), III, p. 361.
- BROWN. J. prakt. Chem. (1839) 17, p. 492.

## LITHIUM AND CARBON.

This carbide has been but recently made. Its formula is  $\text{Li}_2\text{C}_2$ .  $\text{LiCO}_3 + 4\text{C}$ , heated for ten minutes, using a current of 350 amp. and 50 volts, will yield it, or with 950 amp. it may be made in four minutes. A higher temperature than this current produces in the furnace either volatilizes or decomposes this carbide.  $\text{Li}_2\text{C}_2$  forms shining crystals, sp. gr. = 1.65 at  $18^\circ\text{C}$ . Decomposed by moist air and water,  $\text{C}_2\text{H}_2$  being formed. It is easily broken up and is not so hard as glass. Burns in the cold in Cl or Fl, and by gentle heating in Br or I. Concentrated acids have little effect upon it. In hot water the decomposition is quite violent.

## LITERATURE.

- MOISSAN. Sur le carbure de lithium. C. R. 122, p. 362, or Chem. Centrbl. (1896) 67, pt. 1, p. 685, or Abs. J. Chem. Soc. (1896) 70, pt. 2, p. 419.
- MOISSAN. Errata se rapportant à cette communication. C. R. (1896) p. 496.

## MAGNESIUM AND CARBON.

In Dammer's Anorg. Chem. it is stated that magnesium heated in benzol vapors yields a dark mass of this composition,  $\text{MgC}_2$ . No such compound has been made in the electric furnace. The reference given does not mention a definite compound of Mg and C.

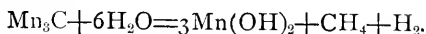
## LITERATURE.

- PARKINSON. Behavior of magnesium with non-metallic elements. J. Chem. Soc. (London) (1867) vol. 20, p. 125.
- GMELIN-KRAUT. (?)
- DAMMER. Handbuch der anorganischen Chemie, Vol. II, 2 (1893).



## MANGANESE AND CARBON.

Troost and Hautefeuille are the discoverers of the carbide whose formula is  $\text{Mn}_3\text{C}$ . This carbide was also produced by Moissan; he stated that with a current of 900 amp. and 50 volts the reduction is practically instantaneous, while with the same voltage and 350 amp. only five to six minutes' heating is necessary.  $\text{Mn}_3\text{C}$  has a sp. gr. of 6.89. Fl attacks it cold and Cl by gentle heating. It burns in oxygen at a low temperature. When decomposed by water there result equal parts of  $\text{CH}_4$  and  $\text{H}_2$ . The equation is:—



No fluid or liquid hydrocarbons are produced. In some early references mention is made of  $\text{MnC}$  and  $\text{Mn}_2\text{C}$ .

## LITERATURE.

- BROWN. [ $\text{MnC}$ ] Ueber Kohlenmetalle. J. prakt. Chem. (1839) 17, p. 492.  
 GMELIN. [ $\text{Mn}_2\text{C}$  and  $\text{MnC}$ ] Handbook of Chemistry (Watt's trans., 1849), IV, p. 213.  
 GMELIN-KRAUT. [ $\text{MnC}_2$ ] (1882) II, 2.  
 MENDELEEF. Principles of Chemistry, I, p. 65 (note 19); II, p. 112-3.  
 TROOST and HAUTEFEUILLE. [ $\text{Mn}_3\text{C}$ ] Etude calorifique sur les carbures de fer et de manganèse. Ann. de chim. (1876) [5] 9, p. 60, or Jsb. Chem. (1876) p. 87, and C. R. (1875) 80, p. 964, and Sur les fontes manganésifères, C. R. (1875) 80, p. 909.  
 ARNOLD and READ. Trans. J. Chem. Soc. (London) (1894) 65, p. 788.  
 DE BENNEVILLE. A study of some alloys with iron carbides. J. Iron and Steel Inst. (London) (1896) no. 1.  
 MOISSAN. Sur la préparation rapide du chrome et du manganèse à haute température. Bull. Soc. Chim. (1894) [3] 11, p. 13.  
 MOISSAN. Sur le carbure de manganèse [ $\text{Mn}_3\text{C}$ ]. C. R. (1896) 122, p. 421, or Bull. Soc. Chim. (1896) [3] 16, p. 1266; Abs. J. Chem. Soc. (1896) 70, pt. 2, p. 423, and Chem. Centrbl. (1896) 67, pt. 1, p. 741.

## MERCURY AND CARBON.

A mercury acetylid is formed in several ways. It results as a heavy white powder by passing  $\text{C}_2\text{H}_2$  through freshly precipitated mercuric oxide suspended in water. Several days are required to prepare it. Sp. gr. = 5.3. Insoluble in  $\text{H}_2\text{O}$ , alcohol, and ether. Slowly decomposed by gradual heating above  $110^\circ$  into Hg and C. The compound explodes by rapid heating or by a blow. Its formula seems to be  $3\text{HgC}_2 + \text{H}_2\text{O}$ . Keiser gives  $\text{HgC}_2$ .

## LITERATURE.

- PLIMPTON and TRAVERS. Metallic derivatives of acetylene. J. Chem. Soc. (London) 65, p. 264. See also  
 BERTHELOT. Ann. de chim. [4] 9, p. 386.  
 BASSET. Chem. News, 19, p. 28.  
 KEISER. Am. Chem. J. 15, p. 535. See also  
 KUTSCHEROW. Ber. d. Chem. Ges. 17, p. 13.

## MOLYBDENUM AND CARBON.

$\text{Mo}_2\text{C}$  is best prepared by heating together 5 pts.  $\text{MoO}_2$  and 1 pt. C for eight to ten minutes in a carbon crucible. 800 amp. and 50 volts is sufficient current. The carbide shows a brilliant, crystalline fracture, exhibits easy cleavage; sp. gr. 8.9. If this carbide is heated with an excess of molybdenum dioxide, molybdenum is produced, and inversely, fused molybdenum readily takes up considerable carbon.

## LITERATURE.

- MOISSAN. Préparation au four électrique de quelques métaux réfractaires; tungstène, molybdène, vanadium. C. R. 116, p. 1225, or Abs. J. Chem. Soc. (1893) 64, pt. 2, p. 471, or Bull. Soc. Chim. [3] 11, p. 857.
- MOISSAN. Préparation et propriétés du molybdène pur fondu. C. R. (1895) 120, p. 1320, or Abs. J. Chem. Soc. (1895) 68, pt. 2, p. 497, or Bull. Soc. Chim. (1895) [3] 13, p. 967.

## NICKEL AND CARBON.

Nickel and carbon act in many ways like iron and carbon. By heating  $4\text{Ni}(\text{CN})_2 + 3\text{H}_2\text{O}$  under proper conditions carbon-containing nickel results. (See Dammer.) When carbon monoxide is passed over finely divided nickel at a temperature between  $300^\circ$  and  $350^\circ\text{C}$ , there results a black powder consisting of Ni and C, varying with the temperature at which the operation was conducted. Ni is said to act in the same way with certain hydrocarbon gases.

## LITERATURE.

- DÖBEREINER. N. J. der Pharm. [Trommsdorff, 1820 (?)] 4, pp. 1 and 293.
- ROSS and IRVING. Ann. Phil. (1862) p. 149.
- MOND, LANGER and QUINCKE. [Action of CO on Ni] Trans. J. Chem. Soc. (1890) vol. 57, p. 749, Chem. News (62) p. 97.
- See also GAUTIER and HALLOPEAU. C. R. (1889) 108, p. 1111.
- MOND and LANGER. D. R. P. 51,572, 14/6, 1889; Patentblatt (11), p. 356; Chem. Centrbl. (1890) II, p. 32.
- MOISSAN (foot-note). Bull. Soc. Chim. (1894) [3] 11, p. 13.

## PALLADIUM AND CARBON.

According to Moissan palladium forms no carbide in the electric furnace. Other chemists mention a carbide of palladium.

## LITERATURE.

- WÖHLER. Ueber die Wirkung des Palladium auf die Weingeist Flamme. (Pogg.) Ann. der. Phys. 3, p. 71. See also
- H. B. MILLER. Ann. Phil. 28, p. 20, and
- BERZELIUS. Lehrbuch der Chemie (1836), III, p. 249, and
- MOISSAN. Sur la solubilité du carbone dans le rhodium, l'iridium et le palladium. C. R. 123, p. 16, or Bull. Soc. Chim. (1896) [3] 16, p. 1292.
- MOISSAN. Research on the metallic carbides. Chem. News, 74, p. 15.

## PLATINUM AND CARBON.

No platinum carbide has been produced by Moissan in his electric furnace. Pt at that temperature takes up some carbon, but upon cooling gives it up as graphite and without forming a definite compound.  $\text{PtC}_2$  is mentioned in a number of chemical publications, as is also  $\text{PtS}_2\text{C}$ . This platinum sulphocarbide is produced by leading a stream of H or N saturated with  $\text{CS}_2$  vapors over spongy platinum at a temperature somewhat below dark red heat. The product is black and finely divided, neither HCl or  $\text{HNO}_3$  attacks it and aqua regia is almost without effect. Heated in a stream of oxygen,  $\text{SO}_2$ ,  $\text{CO}_2$ , and Pt result.

## LITERATURE.

- ZEISE. [ $\text{PtC}_2$ ] Ueber Acechlorplatin, nebst Bemerkungen über einige andere Products der Einwirkung zwischen Platinchlorid und Aceton. J. prakt. Chem. (1840) 20, p. 209.  
 GMELIN. (Watt's trans., 1849) Handbook of Chemistry, VI, p. 146.  
 FISCHER. Kastner's Archiv, 14, p. 148.  
 SCHÜTZENBERGER. [ $\text{PtS}_2\text{C}$ ] Sur un sulpho-carbure de platine. C. R. (1890) 111, p. 391.

## POTASSIUM AND CARBON.

$\text{K}_2\text{C}_2$  is formed by the direct action of carbon and potassium at a red heat. It is decomposed by water, yielding acetylene. Davy prepared it nearly ninety years ago by means of electric heat, and described his product before a London Society in 1808. He made it from graphite and potassium by heating them together in a glass tube in an atmosphere of hydrogen. The product is described as being somewhat like graphite in appearance, infusible at red heat, taking fire in the air, potassium oxide being formed and leaving a black residue. Strongly effervescent with water, giving off a gas which Davy thought was hydrogen. This is the first carbide of which we find record. Davy repeated his experiments, using potassium and willow charcoal.

## LITERATURE.

- GILB. Ann. (1810) 35, p. 433.  
 DAVY. Ueber Kohlenstoffkalium und einen neuen Doppelt-Kohlenwasserstoff. Ann. der Pharm. (1837) 23, p. 144.  
 BERZELIUS. Lehrbuch der Chemie (1836), II, p. 315, and (1844), II, p. 84.  
 GMELIN. (Watt's trans., 1849) Handbook of Chemistry, III, p. 17.  
 BERTHELOT. Sur une nouvelle classe de radicaux métalliques composés. Bull. Soc. Chim. (1866) V, p. 182, and Ann. Chem. 139, p. 150, and Jsb. Chem. (1866) p. 514.

## RHODIUM AND CARBON.

Moissan states that the metals of this group, Rd, Ir, Pd, and Pt, form no carbides in the electric furnace; for, while these metals dissolve carbon readily under such conditions, they give it up in the form of graphite upon solidifying, no carbide resulting.

## LITERATURE.

- MOISSAN. Sur le solubilité du carbone dans le rhodium, l'iridium, et le palladium. C. R. 123, p. 16, or Bull. Soc. Chim. (1896) [3] 16, p. 1292; Abs. J. Chem. Soc. (1896) 70, pt. 2, p. 609. *See also* Abs. J. Chem. Soc. (1893) p. 320.
- MOISSAN. Research on the metallic carbides. Chem. News (1896) 74, p. 15.

## SILICON AND CARBON.

The compound of carbon and silicon known as carborundum (CSi) is of great commercial value, being a good abrasive. Its hardness is between that of corundum and the diamond. A compound is mentioned by Colson which has the formula  $C_2Si$ , and a doubtful compound  $C_7Si_2Al$  is also mentioned in chemical literature.

On a large scale carborundum is made from coke and sand, these being mixed with salt and sawdust before submitting to the electric heat. The charge is put in a long box-shaped furnace surrounding a coarse carbon core which extends between the electrodes. These are from six to eight feet apart, from one to nine carbons being in each end of the furnace. The current passes from eight to ten hours. CSi forms long needle-shaped crystals usually of a greenish-yellow color, sometimes blue. It is unacted upon by mineral acids, decomposed by fusion with alkalis, and oxidizable by  $PbCrO_4$ . The crystals are infusible except in the electric arc. An amorphous product of about the same composition is formed at some distance from the carbon core and beyond the zone in which the crystalline product is found.

The patents for making carborundum are owned by Mr. Acheson in this country and in a number of European countries. It is found to be very useful as an abrasive, and its introduction into the mechanical arts has been rapid.

The di-carbide of silicon, of Colson, is made by passing a stream of  $C_2H_4$  or  $H_2$  saturated with benzine vapors over silicon for several hours. The silicon is contained in a porcelain tube and heated to a bright heat during the conduction of the gas.  $SiC_2$  is decomposed by KOH or by a mixture of  $PbCrO_4$  and  $PbO$ , but is not acted upon even at red heat by acids, oxygen, or chlorine.

Tetra-silico-carbo-sulphide,  $Si_4C_4S$ , is formed by conducting  $CS_2$  vapors over white-hot silicon contained in a porcelain vessel. Other products are produced at the same time, and hence the contents of the dish are treated with hot KOH solution, and with HF. After this treatment the above compound remains as a greenish powder, decomposable by boiling HF,  $H_2S$  being evolved. It oxidizes to  $Si_2C_2O$ .

Silicon nitro-carbide ( $C_2Si_2N$ ) results when Si is heated in the presence of C and N, or in cyanogen, or in the presence of certain carbonaceous substances in an atmosphere of nitrogen.

## LITERATURE (CSi).

- GMELIN. (Watt's trans., 1849), Handbook of Chemistry (CSi?), III, p. 359.
- SCHÜTZENBERGER. Contributions à l'histoire des composés carbosiliciques. C. R. (1892) 114, p. 1089.
- ACHESON. Production of artificial crystalline carbonaceous materials. U. S. pat. 492,767 (Feb. 1893). Reissue, 11,473, Feb. 1895.
- ACHESON. D. R. P. 76,629.
- ACHESON. Carborundum, Its History, Manufacture and Uses. J. Frankl. Inst., Sept. 1893.
- ACHESON. Oesterr. Ztschr. f. Berg- u. Hüttenwesen (1894), 421, p. 115.
- MOISSAN. Sur la volatilisation de la silice et de la zircone et sur la réduction de ces composés par le charbon. C. R. (1893) 116, p. 1222, or Abs. J. Chem. Soc. (1893) 64, pt. 2, p. 532.
- MOISSAN. Préparation et propriétés du siliciure de carbone cristallisé. C. R. (1893) 117, p. 425, or Bull. Soc. Chim. [3] 11, p. 995, or Abs. J. Chem. Soc. (1894) 66, pt. 2, p. 43, or Chem. Centrbl. (1893) pt. 2, p. 909.
- MOISSAN. Action de l'arc électrique sur le diamant, le bor amorphe, et le silicium cristallisé. C. R. 117, p. 423, or Chem. Centrbl. (1893) 64, pt. 2, p. 909, or Abs. J. Chem. Soc. (1894) 66, pt. 2, p. 42, or Bull. Soc. Chim. [3] 11, pp. 863 and 993.
- MOISSAN. C. R. (1895) p. 1393, or Abs. J. Chem. Soc. 68, pt. 2, p. 497.
- MÜHLHÄUSER. On carborundum. J. Am. Chem. Soc. (1893) 15, p. 411.
- MÜHLHÄUSER. Ztschr. angew. Chem. (1893) p. 484; (on analysis of CSi) p. 641.
- MÜHLHÄUSER. Ztschr. anorg. Chem. 5, p. 105, or Chem. Centrbl. (1893), 64, pt. 2, p. 933, or Abs. J. Chem. Soc. (1894) 66, pt. 2, p. 42.
- MATHEWS. Carborundum; Its history, physical properties, and chemistry. School Mines Q. (N. Y.) (1894) v. 16, or Am. Drug. and Pharm. Rec. (1895) or J. Soc. Chem. Ind. (1895) 14, p. 755.
- VOLKMANN. Das Carborundum. Oesterr. Ztschr. f. Berg- u. Hüttenwesen (1894), 42, p. 7 and p. 115.
- BECKE. Beitrag zur Kenntniss der Carborundumkrystalle. Ztschr. Krystall. 24, p. 537, or Chem. Centrbl. (1895) 66, pt. 2, p. 959.
- LURMAN. Siliciumkohlenstoff u. Ferrosilicium. Ztschr. Elektrochem. (1896) III, p. 113.
- MOISSAN. Ann. de Chim. [7] 9, p. 289, or Chem. Centrbl. (1896) pt. 2, p. 1080.
- See also these:—*
- KUNZ. (Note on hardness) Am. J. Sci. 46, p. 471.
- ROTHWELL. (Statistics of production) Mineral Industry (N. Y. 1893).
- HALLER. L'Industrie chimique (Paris, 1895), p. 332.
- Ztschr. Angew. Chem. (1894) p. 118.
- ACHESON. Electric furnace, U. S. pat. 560,291, May 19, 1896.
- DAMMER. (C<sub>7</sub>Si<sub>2</sub>Al?) Handbuch der anorganischen Chemie, II, 1, p. 546.
- COLSON. (C<sub>2</sub>Si) Bull. Soc. Chim. (1882) [2] 38, p. 56, or Jsb. Chem. (foot-note) (1882) p. 257.
- COLSON and SCHÜTZENBERGER. (C<sub>2</sub>Si<sub>2</sub>N) Sur le Silicium. C. R. (1881) 92, p. 1508, or Jsb. Chem. (1881) p. 202.
- COLSON. (Si<sub>4</sub>SC<sub>4</sub>) Sur de nouveaux composés carbosilicés. C. R. (1882) 94, p. 1316.
- COLSON. Action du sulfure de carbone sur le silicium. C. R. (1882) 94, p. 1526, or Bull. Soc. Chim. (1882) [2] 38, p. 56.

## SILVER AND CARBON.

Gay-Lussac states that when silver is melted with lamp-black in a crucible, about three per cent. of carbon is taken up and Ag<sub>4</sub>C is formed. Ag<sub>2</sub>C results by heating the silver salt of cuminic acid [C<sub>6</sub>H<sub>4</sub>(C<sub>3</sub>H<sub>7</sub>)(COOAg)],

in an open dish. It is a yellowish substance, not decomposed by heat. It contains 5.52% C, which remains when this carbide is treated with  $\text{HNO}_3$  (Gerhardt and Cahours).

$\text{Ag}_2\text{C}_2$  is said to result by long heating of the silver salt of pyroracemic acid ( $\text{CH}_3\text{COCOOAg}$ ). It is a gray powder of metallic appearance, containing about 10.51% C. The same compound results from the silver salt of maleic acid [ $\text{C}_2\text{H}_2(\text{COOAg})_2$ ]. This carbide is produced by passing acetylene gas through ammoniacal silver solutions. It is very unstable and difficult to work with. See Keiser's and Plimpton's work.

#### LITERATURE.

- BROWN. J. prakt. Chem. (1839) 17, p. 492.  
 LIEBIG and REDTENBACHEN. [ $\text{Ag}_2\text{C}$ ] Ueber das Atomgewicht des Kohlenstoffs. Ann. Chem. 38, p. 129.  
 BEHAL. Bull. Soc. Chim. 49, p. 335, and Ber. d. Chem. Ges. 21, ref. 609.  
 BERZELIUS. (Foot-note) Pogg. Ann. der Phys. 36, p. 28.  
 GERHARDT and CAHOURS. (?)  
 GAY-LUSSAC. (?)  
 BEREND. [ $\text{C}_2\text{Ag}_2$ ] Ueber einiger neue Derivate des Acetylens. Ann. Chem. 135, p. 257.  
 REGNAULT. (Maleic acid) Untersuchung einiger ihrer Salze. Ann. der. Pharm. 19, p. 153.  
 PLIMPTON. On silver acetylide. Proc. J. Chem. Soc. (1892) p. 109.  
 KEISER. Am. Chem. J. 14, p. 285, or Abs. J. Chem. Soc. 62, p. 1416; see also Ann. Chem. 118, p. 330.

#### SODIUM AND CARBON.

$\text{C}_2\text{HNa}$  and  $\text{C}_2\text{Na}_2$  result by passing acetylene gas over sodium at a dark red heat.  $\text{C}_2\text{Na}_2$  is decomposed by water yielding acetylene.

#### LITERATURE.

- BERTHELOT. Sur une nouvelle classe de radicaux métalliques composés. Bull. Soc. Chim. (1866) V, p. 182, and Ann. Chem. 139, p. 150, and Jsb. Chem. (1866) p. 514.  
 FORGRAND. Chaleur de formation de l'acétylure de sodium. C. R. 120, p. 1215, and Bull. Soc. Chim. (1895), [3], 13, p. 996.

#### STRONTIUM AND CARBON.

$\text{SrC}_2$  forms under about the same conditions obtaining in the production of Ca or Ba carbides. It forms a dark mass, with yellowish fracture; sp. gr. = 3.19; with dilute acids and water it decomposes, giving off chiefly acetylene. Reacts with halogens, oxygen, and sulphur at high temperatures, but not with nitrogen, silicon, or boron. Both  $\text{SrO}$  and  $\text{SrCO}_3$  have been used in making  $\text{SrC}_2$ , and a current of 350 amp. and 70 volts employed.

#### LITERATURE.

- MOISSAN. Etude des acétylures cristallisés de baryum et de strontium. C. R. 118, p. 683, or Bull. Soc. Chim. [3] 11, p. 1007, or Chem. Centrbl. (1894) 65, pt. 1, p. 856.  
 BULLIER. D. R. P. 77,168.

## THORIUM AND CARBON.

$\text{ThC}_2$  is made from thorium oxide, the reduction being more easily effected than is the case in preparing zirconium carbide from zircon.  $\text{ThC}_2$  is decomposed by water,  $\text{H}_2$  and hydrocarbons being formed. Moist air, also, slowly decomposes thorium carbide, sp. gr. = 10.15. Burns at a red heat. Concentrated acids are almost without action upon it. The gases are evolved in about the following percentages:  $\text{C}_2\text{H}_2$  (48.44),  $\text{CH}_4$  (27.69),  $\text{C}_2\text{H}_4$  (5.64), and  $\text{H}_2$  (18.23).

## LITERATURE.

- TROOST. Sur la préparation du zirconium et du thorium. C. R. 116, p. 1227, or Abs. J. Chem. Soc. (1893) 64, pt. 2, p. 473.  
 MOISSAN et ETARD. Sur les carbures d'yttrium et de thorium. C. R. 122, p. 573, or Abs. J. Chem. Soc. (1896) 70, pt. 2, p. 422, or Bull. Soc. Chim. (1896) [3] 16, p. 1271.

## TITANIUM AND CARBON.

$\text{TiC}$  is produced by heating together  $\text{TiO}_2$  and carbon in the electric arc, but according to conditions a variety of compounds may result, some containing C, Ti, and N. A current of 1000 to 1200 amp. and 70 volts is required for this reduction. The resulting  $\text{TiC}$  has a sp. gr. = 4.25, and occurs either as a crystalline aggregate or a fused mass showing crystalline fracture. This is treated with  $\text{HCl}$  to remove titanium. The carbide takes fire at red heat, burning with so much heat as to raise it to a white heat. One of the combinations of Ti, C, and N that has been studied a good deal has this formula  $\text{Ti}_{10}\text{C}_2\text{N}_8$ . Joly considers this to be a mixture of  $\text{TiN}_2$  and  $\text{TiC}$ . It was discovered in the furnace products from certain titaniferous ores.

LITERATURE ( $\text{TiC}$ ).

- SCHIMMER. Titanium carbide in pig-iron. Chem. News (1887) 55, p. 156, and Ber. d. Chem. Ges. 20, ref. 361, and Jsb. Chem. (1887) p. 2522.  
 VIOLLE. L'industrie électrique (1894), III, v. 568.  
 MOISSAN. Préparation et propriétés du titane. C. R. (1895) 120, p. 290, or Bull. Soc. Chim. (1895) [3] 13, p. 963.  
*Concerning the nitro-carbides, etc., see*  
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 WÖHLER and DEVILLE. Ueber die Affinität zwischen Stickstoff und Titan. Ann. Chem. (1857) 103, p. 230, or Jsb. Chem. (1857) p. 173. *See also*  
 DAMMER, Handbuch der Anorganischen Chemie.

## TUNGSTEN AND CARBON.

$\text{CW}_2$  is made from tungstic acid with an excess of carbon, or in a carbon crucible. The carbon in excess of that required by the formula,

CW<sub>2</sub>, is given up as graphite on cooling. CW<sub>2</sub> is an iron-gray compound, very hard, not decomposed by atmospheric moisture, and of a sp. gr. = 16.06.

## LITERATURE.

- MOISSAN. Préparation au four électrique de quelques métaux réfractaires ; tungstène, molybdène, vanadium. Bull. Soc. Chim. [3] 11, p. 857, and C. R. (1893) 116, p. 1225, or Abs. J. Chem. Soc. (1893) 64, pt. 2, p. 471.  
 MOISSAN. Recherches sur le tungstène. Bull. Soc. Chim. (1896) [3] 16, p. 1289, and C. R. 123, II. p. 13, or Ztschr. Elektrochem. (1896) III, p. 109.

## URANIUM AND CARBON.

Commercial uranium oxide is purified and mixed with sugar-carbon and submitted to the action of a current of 900 amp. and 50 volts for five to ten minutes. The operation is carried on in a carbon crucible. C<sub>3</sub>U<sub>2</sub> is the product ; crystalline ; sp. gr. = 11.28 ; harder than quartz but not as hard as corundum. This carbide is peculiar in its decomposition with water. The reaction must be quite complex, for the products are : H<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, CH<sub>4</sub>, and beside these there are produced hydrocarbons, liquid and solid, boiling between 70° and 200°C. Some of these are unsaturated bodies which will reduce alkaline silver solutions. After distilling off the hydrocarbons mentioned above, a bituminous residue remains. U<sub>2</sub>C<sub>3</sub> burns in Fl by gently heating, also in Cl, O, N<sub>2</sub>O<sub>4</sub>, and Br, at temperatures between 350° and 390°.

## LITERATURE.

- MOISSAN. Etude du carbure d'uranium. C. R. 122, p. 274, or Bull. Soc. Chim. [3] 11, p. 11, or Chem. Centrbl. (1896) 67, pt. 1, p. 640, or Abs. J. Chem. Soc. (1896) 70, pt. 2, p. 364.  
 BULLIER and BIGNON. D. R. P. 77,166, and Ztschr. Angew. Chem. (1894) p. 655.

## VANADIUM AND CARBON.

Vanadium anhydride and sugar-carbon subjected to the action of a current of 900 amp. and 50 volts for nine to ten minutes in the electric furnace yield VaC ; a beautifully crystalline compound, sp. gr. = 5.36, harder than quartz, attacked by HNO<sub>3</sub> in the cold. It burns vigorously in oxygen at a dull red heat. Becomes incandescent if heated to 500° in an atmosphere of Cl.

## LITERATURE.

- MOISSAN. Préparation au four électrique de quelques métaux réfractaires ; tungstène, molybdène, vanadium. C. R. 116, p. 1225, or Abs. J. Chem. Soc. (1893) 64, pt. 2, p. 471, or Bull. Soc. Chim. [3] 11, p. 857.  
 MOISSAN. Etude de la fonte et du carbure de vanadium. C. R. 122, p. 1297, or Abs. J. Chem. Soc. (1896) 70, pt. 2, p. 608, or Ztschr. Elektrochem. (1896) III, p. 92, or Bull. Soc. Chim. (1896) [3], 16, p. 1278.



## YTTRIUM AND CARBON.

Pettersson first made this carbide,  $YC_2$ . It has a specific gravity of 4.13. This carbide is golden yellow on a fresh fracture, but remains so only a short while, as the moisture of the air attacks it. The halogens act upon it in the cold. Readily attacked by acids. Burns in oxygen and in the vapors of sulphur and selenium. In making  $YC_2$  in the electric furnace more heat is required than is necessary in the preparation of cerium carbide. A current of 900 amp. and 50 volts effects the reduction in about six minutes. Vapors of the metal are given off during the operation. Water decomposes it readily, yielding the following gases: —

$C_2H_2$  (71.7%),  $CH_4$  (19%),  $C_2H_4$  (4.8%),  $H_2$  (4.5%).

## LITERATURE.

- O. PETERSSON. Kohlenstoffbindungen von den Metallen der seltenen Erden. Ber. d. Chem. Ges. 28, p. 2419, or Bull. Soc. Chim. (1896) [3] 15, p. 101, or Chem. Centrbl. (1895) 66, pt. 2, p. 960, or Abs. J. Chem. Soc. (1896) 70, pt. 2, p. 25.  
 MOISSAN et ETARD. Sur les carbures d'yttrium et de thorium. Bull. Soc. Chim. (1896) [3] 16, p. 1271, or C. R. 122, p. 573, or Abs. J. Chem. Soc. (1896) 70, pt. 2, p. 422.

## ZINC AND CARBON (?)

A compound of zinc and carbon is of doubtful existence although mentioned in old books on chemistry.

## LITERATURE.

- BERZELIUS (and Gmelin-Kraut), 6th ed. 3, 2, 11.  
 GMEIN. Handbook of Chemistry (Watt's translation) (1849), V, p. 13.  
 BROWN. J. prakt. Chem. (1839) 17, p. 492.

## ZIRCONIUM AND CARBON.

$ZrC$  is produced by heating for ten minutes anhydrous  $ZrO$  and sugar-carbon. A current of 1000 amp. and 50 volts was used by Moissan. Gray metallic appearance, scratches quartz, not decomposed by damp air at  $100^\circ$ . In this it differs from the thorium compound. Burns brilliantly in oxygen at a dull red heat.  $ZrC_2$  is also known (Troost).

## LITERATURE.

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 TROOST. ( $ZrC_2$ ) Sur la préparation du zirconium et du thorium. C. R. 116, p. 1227, or Abs. J. Chem. Soc. (1893) 64, pt. 2, p. 473.  
 MOISSAN. Sur la volatilization de la silice et de la zircone et sur la réduction de ses composés par le charbon. C. R. 116, p. 1222, or Abs. J. Chem. Soc. (1893) 64, pt. 2, p. 532, or Bull. Soc. Chim. [3] 11, p. 863.  
 MOISSAN and LENGFELD. Sur un nouveau carbure de zirconium. C. R. 122, p. 651, or Chem. Centrbl. (1896) 67, pt. 1, p. 887, or Abs. J. Chem. Soc. (1896) 70, pt. 2, p. 428, or Bull. Soc. Chim. (1896) [3] 16, p. 1275.



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[Following each author's name is given a list of all the elements to the literature of whose carbides he has contributed.]

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